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SURVEY DESIGN FOR ASSESSING THE SENSITIVITY OF LAKES TO ACIDIC DEPOSITION

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SURVEY DESIGN FOR ASSESSING THE SENSITIVITY OF LAKES TO ACIDIC DEPOSITION

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ABSTRACT

Estimates of the sampling frequency required to describe annual and seasonal (summer stratification and ice-covered period) chemical concentrations in lake water within a given tolerance of the true mean, with 95% confidence, were made using data collected for three lakes. Visual inspection and Monte Carlo simulation of the data suggest that most parameters approximate a normal distribution and thus simple parametric statistical methods may be applied to lake data. Graphs are presented showing 95% confidence intervals from seasonal means for sample sizes of from one to eight for 12 chemical parameters. These estimates will be useful in planning lake water quality surveys. The effect of sampling season is also discussed.

INTRODUCTION

In order to assess the extent of the aquatic resources sensitive to acidification, it is necessary to characterize lakes over a wide geographic range with respect to important parameters such as alkalinity (acid neutralizing capacity), pH, SO_4, and base cations (Harvey et al. 1981, Dillon et al. 1984, Haines 1981). Characterization of lakes at points in time is also essential information needed to assess temporal changes in the chemistry of lakes. It is particularly important to establish baseline chemical conditions of a large number of lakes in order that future changes can be readily evaluated. However, to place statistically-defined confidence about any chemical characterization, it is necessary to collect more than one sample. On the other hand, it is obviously desirable to collect as few as possible samples with minimal reduction in information. The purpose of this paper is to define the minimum sampling frequency necessary to adequately define lake chemistry with respect to the acidification phenomenon.

This subject has been discussed in general in many papers (eg. Ellis 1980, Ellis and Lacey 1980, Walker 1982, Cotter 1985) and texts, but the specific case of acidification of lakes has not previously been addressed. To estimate the required sample size, past estimates of the variability of a given water body are required. In addition, most statistical methods recommended for water quality surveys require the data fit a normal distribution. Estimation of variance and normality requires relatively large numbers of data. In many cases, acquisition of this information is impractical or not economically feasible.

In this paper, we utilize an existing data base produced as a result of an intensive sampling effort on three representative lakes to develop the statistical considerations necessary for planning a survey of similar lakes with respect to sensitivity to acidification. This included 1) using the estimated variability of the annual chemistry of the three representative lakes to determine the minimum sampling frequency necessary to adequately define lake chemistry and 2) assessing the relative accuracy of 1 random sample to estimate the annual mean. In addition the data were used to 3) estimate the distribution of the selected water parameters and test, using a Monte Carlo simulation, the normal distribution assumption and thus the applicability of parametric statistical methods. Since many sampling programmes are designed to establish annual means but are restricted to sampling only seasonally, we used our data set to 4) test whether seasonal means were significantly different from annual means, and 5) assess the potential bias with estimating annual means from one seasonal sample.

STUDY SITE

The lakes discussed here have been intensively studied since 1976. All are in the Muskoka/Haliburton region of Ontario, about 200 km north of Toronto and 200 km southeast of Sudbury, the closest centres of industrial activity. They are in a zone of high deposition of atmospherically-transported strong acid and sulphate (Dillon et al. 1978, Likens and Butler 1981, Dillon et al. 1988), but none receive pollutants directly from point sources. The three lakes discussed here, Blue Chalk, Chub and Harp, are relatively small (Table 1), but typical in size of the approximately 12,000 lakes in this region (Cox 1978).

Their use is primarily recreational with seasonally-occupied dwellings on the shores of all 3 lakes.

The study lakes are situated on the Precambrian Canadian Shield, in a heterogeneous area of metamorphic, plutonic and volcanic silicate bedrock. The unconsolidated surficial deposits in these lakes' watersheds consist of sub-glacially deposited tills of variable thickness, with some accumulation of sand and gravel deposited by glacial meltwaters, and of organic matter (peat) in poorly drained areas. The catchments of the 3 lakes each have areas with relatively thick till, with deposits in the Harp Lake catchment known to reach >10m. Thus, the 3 lakes are considered to be somewhat less sensitive to acidification than those lakes in the high deposition zone with entire catchments covered by only very thin till.

Lakes similar to these three (or less sensitive) constitute ~70% of the sample of about 2000 lakes surveyed in the high deposition portion of Precambrian southern Ontario (Neary et al. 1989). Lakes that are not highly sensitive to acidic deposition were deliberately chosen for this analysis to minimize or eliminate long-term trends in chemistry. To test this, time trend analysis was used (reported elsewhere: Dillon et al. 1987, Dillon unpubl. studies) to demonstrate that there were either no or extremely slight (in the case of SO_4^{2-}) long-term trends in the chemical parameters reported in this study for any of the 3 lakes over the years in question.

METHODS

i) Parameter selection

In order to characterize lakes with respect to their sensitivity to acidification, 12 parameters were considered important.

Alkalinity, the acid neutralizing capacity (ANC) of the water, is probably most important, particularly since it is, unlike pH, conservative with respect to CO_2 concentrations. Biological organisms, however, respond to ambient pH rather than ANC (Mierle et al. 1986). The SO_4 content is an indication of the importance of long-range transport of sulphuric acid and its precursors, since the 'background' or natural SO_4 level in lakes in this region is low (Neary and Dillon 1988). It is also a mobile anion with respect to flux through lakes' catchments, and this controls to a large degree the extent and rate of acidification of aquatic systems (Reuss and Johnson 1986). The cations Ca, Mg, Na, and K are products of weathering and ion exchange processes, which are believed to occur at an increased rate in areas affected by acidic deposition. Dissolved organic carbon (DOC) and colour are strongly related to the organic acid content of natural waters, and indicate qualitatively the importance of naturally occurring organic acids. Aluminum is important because of its toxicological effects on fish and other organisms. Chloride is often chosen as a conservative element generally believed to be largely unaffected by acidic deposition, and is only rarely a significant component of the atmospheric acids. Conductivity, a measure of the total ionic strength of the water, provides a general measure of how 'dilute' the water is. Although nitrate and ammonium are significant components of the

atmospheric deposition in eastern North America, they are not included here because of their biological reactivity; levels measured in lakes are not, in general, indicative of input rates.

ii) Sampling Frequency

Water samples were taken for chemical analysis from Blue Chalk, Harp and Chub Lakes from 1976 to 1985 as part of an investigation of these three lakes and their watersheds. The lakes were generally sampled bi-weekly (twice per month), more frequently at spring and fall overturns, and less frequently in winter, with the exception that during the years 1977 to 1981, the lakes were visited every week during the summer period. The number of samples taken under ice cover varied from 3 to 8 with 4 visits being the average, i.e. approximately one sample per month. The lowest number of samples per year was 20 and 21 visits per lake in the hydrologic years 1982-83 and 1983-84. The most frequently sampled hydrologic year was 1977-78 with 31, 35 and 36 visits respectively to Blue Chalk, Harp and Chub Lakes.

iii) Sampling Technique

Samples were collected at the deepest spot in each lake. A peristaltic pump and Tygon tubing were used to obtain water at 2 m intervals commencing at 1 m below the surface to 1 m above the bottom. Aliquots from all depths were combined such that a single volume-weighted composite sample was obtained for each of the epilimnion, metalimnion and hypolimnion during the period of thermal stratification. These three

samples were analyzed separately for chemical parameters. Under conditions of thermal homogeneity, water from all depths was pooled to give a single volume-weighted sample representative of the entire lake. Sample containers were filled by pouring the composite water through 80 uM Nitex mesh to remove coarse particulate material. A complete description of sampling methods is available in Scheider et al. (1983) and Locke and Scott (1986).

iv) Analytical Methodology

Chemical analyses were performed at Dorset or Toronto, depending on the perishability of the parameter. All analytical techniques are described in Ontario Ministry of the Environment (1983) and the laboratory performance is reported in Ontario Ministry of the Environment (1986). The analytical method used and the average analytical standard deviation based on replicate samples and standards are summarized in Table 2 for the 12 chemical parameters considered in this paper.

The methodology for 7 of the 12 parameters (Al, Ca, Mg, Na, K, Conductivity, pH) did not change significantly over the course of this study. Method alterations for 3 parameters (Cl, DOC, and Colour) did not result in any systematic differences before and after the changes, as shown by intercomparison of methods. Alkalinity was measured by titration to the equivalence point (Gran titration) from July 1979. Prior to this date, titration to a fixed end-point (pH 4.5) that was lower than the equivalence point (usually pH 4.8-5.1) was carried out routinely. Although there is a defined relationship between the

two titration results (Harvey et al. 1981, Henriksen 1982), we have used only those data collected by the Gran Method.

Sulphate was measured by the methylthymol blue (MTB) method to June 1980 and by ion chromatography thereafter. Because of a significant colour interference with the MTB method (Kerekes 1984), only the results obtained after June 1980 are considered here.

v) Statistical Methods

Data Reduction

The analytical results of the individual samples collected on each date were edited to delete obviously incorrect values using the principles of charge balance, the relationship between ionic strength and conductivity and the theoretical relationships between pH, alkalinity and DIC (Stumm and Morgan 1981). DIC was measured on all samples but the results are not reported here (P. Dillon, unpubl. studies). Less than 2% of the results were discarded in this fashion.

During periods of lake stratification, the chemical results from each strata were volume-weighted according to lake morphometry to give a single value. This data was then pooled annually (AN) and over the whole ten year study (TOT). For some statistical analyses, the data were also pooled by functionally-defined seasons over the whole ten-

year study, including spring overturn (SO), summer stratification (SS), fall overturn (FO), ice free (IF - which includes all of the above) and ice covered (IC).

Sample Distribution

To determine the number of samples required for a given level of statistical confidence, the underlying variance of the sampled population has to be estimated. As there is significant year-to-year variability in these data sets (see below), the best overall estimate of variance about an annual (or seasonal) mean would be the average, over ten years, of the individual annual (or seasonal) variances. However, we decided to be conservative and to over-estimate the variance by using the variance obtained from the ten-year pooled data sets (TOT, SO, SS, FO, IF and IC).

None of these samples were collected randomly over time. Rather a systematic sampling strategy was employed, primarily because of the expected seasonal trends in some parameters. These seasonal trends as well as the significant within-year similarity (as opposed to between years) causes serial dependence in the data. When all samples are lumped together, dependencies of this sort can distort the sampling distribution and make the estimation of sample size for a given confidence level problematic. Nonetheless, we will assume that the ten-year pooled data sets consist of approximately independent and identically distributed variates.

Given the variance of a Normal sample distribution, the calculation of required sample size is straightforward. However if the distribution is non-normal, alternative

procedures must be used. We tested the fit of the annual data and the two non-overlapping seasonal data sets with the greatest sample size (SS and IC) to the normal distribution using Lilliefor's test (Conover 1971). In addition, we compared, for a given sample size, the estimated confidence intervals about the annual mean obtained with the normal approximation to those obtained with a Monte Carlo approximation that makes no assumption about sample distribution.

The Normal Approximation

The normal approximation for an interval 'L' about the mean, within which observations will fall 95% of the time (Snedecor and Cochran 1980) is:

$$L = 1.96\ S\ /\ \sqrt{n}$$

where S = population standard error

n = number of samples

We used the sample standard deviations as an approximation of the population value. The simple calculation for L was made on n = 1 to 8 for the annual data (AN) and the two seasons (SS and IC).

For comparison a binomial test, which makes no assumptions about the distribution of the samples, was used to estimate sample size (Cotter 1985Stumm

Monte Carlo Comparison

The 95% confidence interval 'L' estimated with the normal approximation was compared with a Monte Carlo simulation. The simulation drew every possible combination, without replacement, of the specific sample size (n = 1 to 3). The distance 'L' of the 95% confidence interval was set as an upper and lower boundary about the mean and the number of simulated means falling beyond each boundary was counted. Expressed as a percent of the total number of cases, the count was compared to the normal 95% confidence interval.

RESULTS

i) Descriptive Chemistry

1) Annual Means

The three lakes represent a range of chemical composition normally observed on Precambrian terrain in much of Ontario (Table 3). All are dilute lakes (mean conductivity over 10 years ranged from 29.7 to 35.3 μS) with low levels of major ions. Blue Chalk lake is a very clear lake (colour = 6.0 Hazen units) with low dissolved organic carbon (DOC = 1.8 mg l^{-1}) and moderate alkalinity (4.0 mg l^{-1} as $CaCO_3$). Harp Lake is intermediate in color (21.1 Hazen units) and DOC (4.1 mg l^{-1}) and also low alkalinity (3.2 mg l^{-1} as $CaCO_3$). Chub lake is a coloured (dystrophic) lake (46.5 Hazen units) with a DOC value

of 4.9 mg l^{-1} and very low alkalinity (0.70 mg l^{-1} as $CaCO_3$). Chub Lake has the highest average Al concentration (96 $\mu g\ l^{-1}$) and lowest average pH value (5.66) of the study lakes.

2) Seasonal Variability

The average seasonal values and the annual average for each parameter for the three lakes are shown in Fig. 1-3. The measured standard deviations and means for each parameter for annual and each of two seasons (SS and IC) are summarized in Table 3. In addition, the annual and seasonal means for each year were matched and compared over all ten years using the Wilcoxon matched pairs signed rank test and are shown in Table 4.

There appears to be little seasonal bias compared to the annual means as only a few parameters showed any significant ($p<0.05$) seasonal trend (Fig. 1 to 3 and Table 4). Most of the differences between the long term seasonal and annual means were less than the analytical standard deviation (Table 4).

The summer-stratified and ice-cover seasons encompass the majority of the sample dates used to calculate the annual mean and, not surprisingly, both are close to the annual mean value (Table 3). The ice free season (IF) is included here because lake surveys may be conducted in which the thermal condition in specific lakes are not measured. It appears that there is no significant difference between IF and the annual means for most of the parameters in the three lakes (Table 4). Some general trends are apparent, however. Na, and possibly Mg, concentrations tended to be greater than the annual mean during most SS seasons in all three lakes and less during the IC season. Five of the 12 parameters were

consistently lower or higher than the annual mean during the IC season in highly coloured Chub Lake. Some specific seasonal trends of differences will be discussed further.

For conductivity the seasonal differences were well within the standard deviation (sd) of the analytical methods. All three lakes had their lowest values during the spring overturn (only Blue Chalk significantly different, Δ = -0.7 μS) and the highest values during ice cover (only Chub lake significant, Δ = 0.7 μS).

The pH's of all three lakes were consistently less than the annual average under ice cover and during spring overturn. Blue Chalk lake (pH = 6.59) has consistently lower values during IC (Δ = -0.17) and consistently higher values over the summer season (Δ = 0.04). In contrast, Chub Lake (pH = 5.66) had consistently lower values during fall overturn compared to the annual mean (Δ = 0.09).

Calcium, Cl, Na, K and Mg seasonal mean values were within the analytical standard deviation of the annual mean value. However, despite the small differences in means there is some seasonal trend of consistently lower Na concentrations during SS and higher Na and Mg concentrations during IC compared to annual means over the study period.

For sulphate, the difference between the seasonal means and annual means were generally within the sd of both analytical methods (Table 3). There is a bias to lower than average annual values at spring overturn (Δ = -0.10 to -0.15 mg l^{-1}) and the highest values of the year occurred during IC (Δ = 0.102 to 0.270 mg l^{-1}).

DOC varied little throughout the year for Blue Chalk and Harp Lakes, remaining within the standard deviation of the analytical sd (0.148 mg l^{-1}). In Chub Lake the mean DOC concentrations were consistently lower than during spring (Δ = -0.33 mg $^{-1}$) and consistently higher during ice cover (Δ = 0.24 mg l^{-1}) compared to the annual mean.

Colour varied between seasons differently in the three lakes. Although there was no significant trend, low coloured Blue Chalk Lake (6.0 Hazen units) had lower colour under ice cover in each of the 3 years it was measured and somewhat lower values during the spring overturn. Harp lake, with intermediate colour (21.1 Hazen units) had consistently higher color during IC and slightly higher values during FO. Highly coloured Chub Lake (46.5 Hazen units) had the lowest values during SO and highest values during FO.

ii) Data Distribution

1) Histograms

Histograms of the multi-year data set are presented for each parameter for all three lakes (Fig. 4 to 6). Most of the parameters deviated from normality according to Lilliefor's test (Table 5). The theoretical normal distribution about the mean is marked on the histograms for comparison. Visual inspection reveals that most of the parameters have distributions which approximate the theoretical normal distribution or tend to be leptokurtic (values over-represented around the mean). There are no apparent trends in deviation

from normality for any one parameter or within any one lake. Specific cases are described below.

Conductivity measurements had a leptokurtic distribution about the mean in Blue Chalk and Harp Lakes. Chub Lake has a bimodal distribution with one peak at 27.5 μS and another at 30 μS.

Alkalinity measurements in Chub Lake, which had the lowest mean (0.70 mg $CaCO_3$ l^{-1}), were negatively skewed, i.e. a larger number of values less than the mean with a long tail above the mean. Blue Chalk and Harp Lakes, with moderately low alkalinity, have values distributed more closely to the normal-shaped curve.

pH measurements were somewhat positively skewed for Blue Chalk Lake, while they were close to normal or slightly leptokurtic in Harp and Chub Lakes.

Calcium measurements appear to be close to normally distributed in all three lakes. Chub Lake values are slightly more platykurtic and the other two are slightly leptokurtic in shape. Magnesium is perhaps the most evenly distributed parameter and the distribution is close to the normal curve in all three lakes. Sodium concentrations tended to be negatively skewed in Harp Lake but leptokurtic in the other two lakes. Similarly, potassium has a very peaked distribution in Blue Chalk and Harp Lakes. The stair-casing of alternating high and low frequencies over the range of measurements for the above parameters is probably an artifact of the rounding method used in reporting the values.

The chloride concentrations are close to normally distributed. Blue Chalk Lake had the most peaked distribution with the lowest variability.

Sulphate measurements had slightly different distributions in each of the three lakes. The Chub lake data appears to be bimodal, with one peak at 9.5 and the other around 7.5 mg l^{-1}. In Harp Lake the measurements appeared to be platykurtic about the mean while they appeared to be normally distributed in Blue Chalk Lake.

Harp and Blue Chalk Lakes have leptokurtic distributions of DOC compared to the normal curve, with a slightly negative skew in Harp Lake. Chub Lake DOC concentrations are platykurtic in distribution.

For colour measurements, there are generally more values at the mean than expected by the normal distribution. This is most pronounced in Blue Chalk Lake, which has the lowest mean colour of the three lakes.

There is a large variability in aluminum measurements when all the data is considered. Due to recent improvements in analytical methods, data collected after 1984 will be a more accurate and precise measurement of water concentration. For the entire data set, Al concentrations in Blue Chalk Lake are strongly negatively skewed, while Al concentrations in Harp Lake are only slightly negatively skewed. The distribution of Al values is leptokurtic in shape in Chub Lake.

2) Monte Carlo Comparison

The results from the count of Monte Carlo simulation cases falling beyond the boundaries of the estimated tolerances, with 95% confidence, for a given sample size are shown in Tables 6a to 6l. The results for all 12 parameters generally have counts less than 5%, i.e. very close to the 95%-quantile falling within the parametric confidence boundary. These results tend to verify the normality assumptions and that the parametric statistics are robust enough to be applied to this lake chemistry data. The highest count beyond the 95% C.I. in the Monte Carlo simulation was 10.3% (Na, Harp Lake, IC, Sample size n = 1). The lowest counts were 0% of the cases falling beyond the 95% C.I. This occurred in a number of simulations, all of which were sample size n = 1.

Deviations from the normal approximation for some parameters was indicated by the Monte Carlo simulation results. As was observed from the histograms, the concentrations of Na and alkalinity in Chub Lake were negatively skewed as all or most of the counts were above the upper confidence limit (%> +L). Cl concentrations during ice cover were also negatively skewed and pH was positively skewed in Blue Chalk Lake. An apparent difference between seasons was observed in Harp Lake for colour. The counts suggest colour was positively skewed during the SS period and negatively skewed during the IC period. However, in all the above cases the percentage of counts remained below or near 5%.

- Large deviations from the expected normal distribution are indicated for DOC concentrations in Harp Lake and Al concentrations in all three lakes. DOC concentrations

were negatively skewed, as most counts were beyond the upper 95% confidence interval, with an overall estimated α of 0.056 to 0.083. Similarly, Al concentrations were negatively skewed in all three lakes, very strongly in Blue Chalk, with a relatively large % of the counts outside the 95% C.I. (4.3 to 8.5%).

iii) Sample Size

1) The Normal Approximation

The numbers of samples required to estimate a submean which is within a given distance of the long term mean, with 95% confidence, for the 3 study lakes (calculated from 1976 to 1984) are shown in Tables 7 and 8. The 95% C.I. are expressed as a function of sample size for the two seasons: summer stratified (SS) and ice cover (IC) in Fig. 7.

For most parameters, one random sample would probably be within 20 or 30% of the annual mean for the study lakes. Similarly, sampling frequencies of 1 to 3 per year would produce mean annual estimates within 20% of the long term mean about 95% of the time. The two exceptions are the parameters colour and Al which have large variability about the mean and, thus, require considerably greater sampling effort. To be within 10% of the long term mean, an average calculated from up to 20 samples may be required for the 12 parameters. If a larger confidence interval than 95% is acceptable, then the number of samples can be reduced. The variability associated with seasonal means are comparable to the long term annual means and the similarity in estimated sampling frequency for the given confidence interval (95%) reflects this. Analytical and quality control standard deviations are so small relative to the natural variability that intensive sampling frequencies

would be required to produce estimates as close as the analytical and quality control standard deviations from the long-term mean.

The standard deviations for conductivity are very consistent (range 0.76 to 2.00) for the three lakes and two seasons. One sample, taken any time of the year, would be within 2 to 4 μS, or about 10%, of the long term annual mean.

Similarly the standard deviation for alkalinity are consistently around 0.2 mg l^{-1} and 1 random sample would be within 0.4 to 0.75 mg l^{-1} of the annual mean. A sampling frequency of 2-4 per year would produce estimates within 10% of the long term annual mean. However, the annual mean for Chub Lake is considerably lower. Thus, for dilute Chub Lake a sampling frequency of approximately 10 would be required to be within 20% of the annual mean.

The annual and seasonal variability of pH is consistent between lakes with a standard deviation ranging from 0.139 to 0.198 pH units. One random sample would be within 0.4 units, or about 5%, of the annual mean. A more acceptable tolerance of 0.1 units from the mean would require as many as 8 to 16 samples per year or season. A sampling frequency of 2 to 4 should estimate an annual or seasonal mean within 0.2 units of the actual mean, 95% of the time.

The standard deviation for seasonal and annual means for Ca concentration ranged from 0.247 to 0.389. To get an estimate of seasonal or annual Ca concentration within 10% (0.2 to 0.4 mg l^{-1}) of the mean, 95% of the time you would require 2 to 7 samples. One

or 2 random samples would produce an estimate within 0.5 to 0.7 mg l^{-1}, or about 20%, of the mean. Chub has a more variable Ca distribution in both IC and SS periods.

The variation for Mg is very consistent (standard deviation 0.072 to 0.085 mg l^{-1}) and a sampling frequency of 2 to 5 would produce a seasonal or annual estimate within 10% of the actual mean. One random sample would produce an estimate within about 0.15 mg l^{-1} (20 to 25%) of the actual seasonal or annual mean. Similarly, potassium has a consistent variability for the lakes and seasons considered here (0.044 to 0.066 mg K l^{-1}). Six samples are likely to estimate within the analytical standard deviation (0.04mg l^{-1}) of the seasonal or annual mean. One or 2 samples would estimate within 0.1 mg l^{-1} (20 to 30%) of the annual mean.

The standard deviation of the annual means for Na was consistent between lakes but there appears to be slightly more variability during IC than SS seasons, except in Blue Chalk Lake where it is the same year round. For annual means, approximately 4 to 13 samples and 2 to 3 samples would be required to estimate within 10% (0.07 to 0.10 mg l^{-1}) and 20% of the actual mean, respectively. One random sample would be within about 0.25 mg l^{-1} (20 to 35%) of the actual annual mean. Chub Lake during IC is the most variable example and a slightly greater sampling frequency of about 17 and 4 would be required to estimate within 10% (0.08 mg l^{-1}) and 20% (0.15 mg l^{-1}), respectively, of the actual mean.

Chloride standard deviations are relatively large compared to the means and ranged from 0.060 to 0.131 mg l^{-1}. A sampling frequency of 9 to 25 would be needed to estimate

within 10% of the actual annual mean. Two to 6 samples would estimate within 20% (0.09 to 0.25 mg l^{-1}) of the actual mean 95% of the time. As with Na, there appears to be more variability during IC than SS, except in Harp Lake where it is the same year round. Chub Lake during IC is the most variable example.

The standard deviation for SO_4 was relatively consistent between lakes and seasons, ranging from 0.292 to 0.474 mg l^{-1} for data analyzed by ion chromatography only. The variance is low relative to the long-term mean and 1 or 2 samples would estimate within 10% of the actual annual or seasonal mean.

There is considerable difference in DOC variability between the three lakes. Blue Chalk and Chub Lakes had lower standard deviation and approximately 3 to 7 samples would estimate within 10% of the actual annual mean. Just 1 or 2 samples would be required to estimate within 20% of the annual mean. DOC concentrations in Harp Lake were much more variable relative to the mean. This was primarily due to high variability during SS (0.887 mg l^{-1}) compared to IC (0.341 mg l^{-1}). To estimate within 10% of the actual seasonal mean DOC in Harp Lake, 18 samples would be required during SS compared to 2 or 3 during IC. Just 1 sample during IC would be within 20% of the actual seasonal mean, while it would take 3 or 4 samples during SS to get similar precision.

Both colour and Al have a large standard deviation relative to the annual and seasonal mean in all three study lakes. An intensive sampling regime would be required to have acceptable precision on estimates of average concentrations. Greater than 10 samples for colour and 30 samples for Al would be required to estimate within 10% of the

annual or seasonal mean. One random sample would be greater than 35% and 50% of the actual mean for colour and Al, respectively. The relative variability does decrease as the colour or Al concentration increases. In highly colored Chub Lake approximately 3 to 5 samples would estimate within 20% of the actual mean. Chub Lake also had the highest Al concentration, but at least 7 samples would be required to estimate within 20% of the actual annual or seasonal mean.

2) Non-parametric Estimates

An attempt was made to estimate the lowest number of samples required based on the 95% quantile and the binomial distribution (Cotter 1985). This method has the advantage of being distribution free. However, the method requires a minimum of 5 to 6 samples to define a confidence limit about a quantile and that appears to be a larger number of samples than required as indicated by the data.

DISCUSSION

i) Assumptions

The practical application of these results require acknowledgement of both the statistical assumptions inherent in the methodology and of what we can call the assumptions resulting from regionalization or extrapolation of the findings.

The statistical methods employed here assume 1) the data are independent and random samples of the true population, and 2) for some of the statistical tests, that the measured values for each parameter are normally distributed; thus, the parametric statistics can be used to estimate u, variance and the sample size required.

As noted earlier, the lakes were not randomly sampled. In practical terms a completely random data set is extremely difficult, if not impossible, to obtain. Systematically sampled data can be treated as random sometimes as long as there is no systematic behaviour related to the parameters measured (Ellis and Lacey 1980). If there is a systematic trend, then it is important that the sampling regime be out of step with any naturally occurring frequency in the lakes if the risk of significant bias is to be avoided. However, it is unlikely that natural variation would be in cycle with a regular 'work week'. In addition the sequence of sampling varied year to year and the irregularity of natural factors would reduce if not prevent alignment with seasonal or perhaps shorter cycles. Thus the multi-year pooled data sets are assumed to represent an intensive random sampling of individual lakes for an average hydrologic year.

The danger or bias of systematic sampling when sampling frequency and natural cycling coincide is that it may artificially reduce estimates of true variance in the population. However, in this study artificially reduced variance would result in a predicted lower sampling frequency needed for a given 95% confidence interval about the mean assuming random sampling. Just how liberal an estimate of required sample size depends on the size of the cycle in relation to the variability of the time interval (i.e. 1 or 2 per month). As

mentioned above, we have assumed that the sampling frequency does not coincide with naturally occurring cycles.

Serial dependence of the data is a common and can be a serious problem in water quality surveys. Generally, temporal correlations in water quality measures are slight if the time interval is relatively large (Millard et al. 1985). However, SS sampling frequencies in this study were often greater than 1 per month and potential serial dependence may prevent the application of a distribution model (Lettenmaier 1976).

If we believe that the multi-year pooled data set represents random samples about a relatively stable long-term mean, then we have a data set large enough to adequately determine sample distribution. The results from the Monte Carlo simulation suggest that most parameters approximate a normal distribution. It appears that the parametric methods employed here are robust enough to accommodate some departure from normality. Other workers have suggested that assuming normal distribution is valid in water quality data as long as one is concerned with arithmetic mean (Montgomery and Hart 1974, Walker 1982). This is, in part, a statement of the central limit theorem that whatever the shape of the frequency distribution of the original population, the distribution of means in repeated random samples of size 'n' tends to become normal as 'n' increases. It would seem that even a low 'n' of 2 or 3 will suffice to make the 2.5 and 97.5 percentiles of the lake chemistry means fall on or near the normal 95% confidence interval boundaries.

Artificial truncation of the distribution by a detection limit may introduce considerable bias. This may be a problem with some of the examined parameters,

especially Al (i.e. Blue Chalk Lake data). Monte Carlo simulations suggest that Al and possibly DOC data deviate substantially from the normal distribution and that perhaps a log-normal transformation should be performed or non-parametric statistics used (Cotter 1985). Care should be taken with any case where a mean concentration is near the detection limit of the analytic method.

Regionalization or extrapolation assumptions concerning the sampling procedure include:

1) the best estimate of the true value for the concentration of the 12 parameters is our volume- weighted annual average for our intensive study lakes,
2) individual samples are a true reflection of water quality at time of sampling,
3) there is no difference in true values of the 12 parameters between years for Blue Chalk, Harp and Chub Lakes and, therefore, the multiple year data set can be lumped to increase sample size,
4) the three intensively studied lakes represent a large number of lakes in this province and results from them may be extrapolated to some range of lakes with similar chemistry and can be useful in determining survey sampling strategies,
5) The discussion only applies to our particular field methods. Other field methods may not have the same variance ie. grab samples vs. volume weighted samples.

The representativeness of a point sample is an important consideration in any study but is beyond the scope of this manuscript. Ellis and Lacey (1980), Walker (1982) and Mar et al. (1986) give relevant discussions concerning this topic.

Lumping the multi-year data set was done to increase the sample size in order to more effectively determine the distribution of the data and population variance. Ideally, approximately 100 samples should have been taken randomly from each lake during one hydrologic year. With multiple years it may be difficult to distinguish between trend and random variation. The three lakes were deliberately chosen because there were little or no annual trends. However, the difference between years will simply increase our estimate of variability and any conclusion drawn from the estimate will tend to be conservative when applied as a within year variability.

The representative nature of the 3 studied lakes to the population of lakes to which the results can be applied is a very important consideration if the results are to be extrapolated to other less intensively studied water bodies. The mean annual concentration of the 12 parameters in the three lakes roughly cover the range found in most lakes in the area. Similar physiographic (including climatic variability) conditions occur over the area and presumably most lakes will have similar within year and between-year variability. Of the lakes in the study area that were sampled frequently enough to estimate variance, most have variances within the range of the three study lakes. These results may also be extrapolated, with some discretion, to other water bodies with similar mean annual concentrations, geologic and physiographic characteristics.

ii) General Remarks

To determine the sampling frequency for a given sampling programme on a lake the following information is required:

1) how much uncertainty can be tolerated, and to what degree of confidence, in the estimate, and

2) what is the variability of the water chemistry.

It appears that most of the examined parameters are roughly normally distributed about the mean annual concentration. If enough data are present to calculate past estimates of variability of a lake, then parametric methods, such as employed here, may be employed to determine the sampling frequency required with reasonable safety. Problems of systematic sampling and serial dependence of the data must still be considered. The exceptions are Al and possibly DOC, which appear to have somewhat skewed distributions in the three lakes studied. However, the variance was considerably high for these two parameters and estimates of sampling frequency were high as well. Considerable skewness may result from truncating when lake water concentrations are near detection limits. In these situations a log-normal approximation or non-parametric methods should be employed.

If adequate information does not exist about the variance of a given lake chemistry then the graphs may be used to estimate the sampling frequency required for a given survey

program to produce estimates within a given tolerance of the true mean with 95% confidence. The graphs depicting the 95% confidence interval as a function of sample size show that the estimates rapidly converge to the true mean from sample sizes one to four, with little improvement beyond that. Provided the lake has similar chemistry and physiographic characteristics to the study lakes these should be reasonable estimates.

Marked seasonal trends occur in most lake water parameters measured in lakes. The results presented here suggest that there is very little difference between various seasons and annual means on the long term. Ellis and Lacey (1980) suggest expressing the systematic time-dependence of concentration as a ratio (within period standard deviation) / (overall standard deviation). The smaller the number the greater the ' benefit' or bias of systematic sampling. The standard deviation of the two seasons with ample data, SS and IC, are as large or larger than the annual variability suggesting little bias on variance estimates in systematically sampling at least on a seasonal basis for these lakes. This is true of conductivity, alkalinity, Ca, Mg, K, and SO_4 where 1 or 2 samples would be within 20%, and often 10%, of the annual mean. Some parameters have consistently lower or higher concentrations, but not significantly so, during certain seasons. This information would be useful in determining when to sample for maximum or minimum annual values.

The annual variability for DOC, Colour and Al was considerable and large sampling frequencies are required to estimate annual and seasonal means with reasonable precision. This is also the case for pH if an acceptable tolerance of 0.1 or 0.2 pH units is considered. Systematic sampling may be employed to separate the unexplained variation and exploit the regularly occurring seasonal cycles in water chemistry in the sampling design (Ellis and

Lacey 1980). It appears that the period of the within-year or seasonal cycles is shorter then the two defined hydrologic seasons (SS and IC) and each season incorporates a large portion of the overall annual variance. Utilizing more detailed information of the within-year cycles in a systematic sampling regime could result in substantial reduction in sampling error and sample size needed for a given precision.

Seasonal trends in water chemistry may be more pronounced in smaller or more sensitive waterbodies, possibly due to the greater interaction with seasonal cycles of runoff chemistry with the surrounding watershed. Chub Lake, which is the most dilute and potentially the most sensitive to acid deposition, consistently had larger variance relative to the annual mean. Seasonal means were also consistently different from the annual means, especially during IC periods. Greater sampling frequency of such lakes or exploitation of seasonal cycles to reduce the required sample size may be necessary for surveys of potentially sensitive lakes.

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Table 1. Location and morphometric features of the study lakes.

	Blue Chalk	Harp	Chub
Latitude/Longitude	45°12'N 78°56'W	45°23'N 79°08'W	45°13'N 78°59'W
Lake Area (km^2)	0.494	0.669	0.322
Watershed Area (km^2)	1.35	5.09	2.86
Mean Depth (m)	8.5	12.4	8.9
Maximum Depth (m)	23	40	27

Table 2. Chemical parameters, standard deviation of the test and analytical method used (Ontario Ministry of the Environment 1983, 1985).

Parameter	Standard Deviation	Method
Cond	0.22 μS	radiometry meter
Alkalinity	0.050 mg L^{-1} $CaCO_3$	inflection point potentiometer titration
pH	0.032 pH	electrometric
Ca	0.151 mg L^{-1}	atomic absorption
Mg	0.042 mg L^{-1}	atomic absorption
Na	0.070 mg L^{-1}	atomic absorption
K	0.040 mg L^{-1}	atomic absorption
Cl	0.051 mg L^{-1}	colourimetry
SO_4	0.536 mg L^{-1}	1976-1980 methylthymol blue colourimetry
	0.167 mg L^{-1}	1980-1985 ion chromatography
DOC	0.148 mg L^{-1}	UV digestion, colourimetry
Colour	0.52 Hazen units	colourimetry
Al (total)	5.3 μg L^{-1}	atomic adsorption

Table 3. Mean values and standard deviations for 12 chemical parameters in three lakes in the annual (AN), summer stratified (SS) and ice-covered (IC) seasons. Values include data collected from 1976 to 1985.

		AN			SS			IC		
Parameter	Lake	N	mean	s.d.	N	mean	s.d.	N	mean	s.d.
Cond	BC	238	29.9	1.35	179	29.9	1.40	38	30.4	1.16
	HP	247	35.3	1.11	176	35.2	0.76	42	35.9	1.81
	CB	244	29.7	1.82	178	29.6	1.74	42	30.6	2.00
Alkalinity	BC	120	3.99	0.369	87	4.00	0.39	19	4.06	0.18
	HP	122	3.21	0.225	87	3.19	0.21	19	3.28	0.22
	CB	116	0.70	0.212	84	0.70	0.22	20	0.70	0.21
pH	BC	238	6.59	0.201	179	6.64	0.198	38	6.42	0.147
	HP	248	6.30	0.145	177	6.32	0.142	42	6.25	0.139
	CB	244	5.66	0.179	179	5.68	0.182	42	5.62	0.183
Ca	BC	201	2.76	0.274	147	2.77	0.286	34	2.74	0.252
	HP	196	3.12	0.260	135	3.11	0.247	33	3.18	0.309
	CB	199	2.68	0.359	138	2.67	0.356	38	2.76	0.389
Mg	BC	200	0.74	0.079	146	0.74	0.081	34	0.75	0.067
	HP	200	0.93	0.080	135	0.94	0.078	37	0.95	0.085
	CB	197	0.68	0.074	135	0.68	0.078	39	0.70	0.072
Na	BC	201	0.78	0.210	148	0.77	0.12	33	0.83	0.11
	HP	202	1.00	0.111	135	0.98	0.10	39	1.06	0.12
	CB	202	0.70	0.124	138	0.68	0.11	41	0.76	0.16
K	BC	201	0.37	0.05	149	0.37	0.05	32	0.38	0.04
	HP	201	0.54	0.05	135	0.53	0.04	39	0.55	0.07
	CB	202	0.40	0.05	138	0.40	0.05	41	0.41	0.06
Cl	BC	204	0.43	0.065	149	0.42	0.060	36	0.46	0.077
	HP	203	0.77	0.118	135	0.77	0.120	40	0.78	0.124
	CB	201	0.49	0.122	137	0.49	0.117	42	0.51	0.131
SO_4	BC	94	6.79	0.453	69	6.79	0.474	15	6.93	0.374
	HP	93	8.08	0.380	65	8.10	0.410	15	8.10	0.292
	CB	93	7.56	0.396	64	7.52	0.393	18	7.74	0.423
DOC	BC	137	1.8	0.227	99	1.9	0.208	23	1.8	0.182
	HP	144	4.1	0.856	96	4.1	0.887	26	4.1	0.341
	CB	129	4.9	0.473	88	4.8	0.450	25	5.1	0.456
Colour	BC	91	6.0	2.37	64	6.8	1.94	17	3.6	1.87
	HP	95	21.1	4.46	65	20.2	4.21	17	23.1	3.45
	CB	90	46.5	8.63	62	45.1	8.01	18	49.5	9.16
0Al	BC	94	11.62	10.80	63	10.53	8.33	19	11.95	12.98
	HP	107	43.19	15.43	68	42.6	16.24	23	40.0	14.74
	CB	111	95.92	26.60	73	93.8	24.28	24	95.9	26.23

Table 4. Comparison of seasonal mean values to the hydrologic year mean and test of significant differences. The nonparametric test used is the Wilcoxon matched-pairs signed-ranks test. Results are reported as the means of the differences (seasonal means-annual mean) and the significance level of the Wilcoxon test. (SO = spring overturn; SS = summer stratified; FO = fall overturn; IC = ice-covered; IF = ice-free; AN = annual).

Parameter	Lake	SO-AN	SS-AN	FO-AN	IC-AN	IF-AN
Cond	BC	- 0.7 *	- 0.1	- 0.4	0.4	- 0.1
	HP	- 0.6	- 0.0	- 0.3	0.3	0.0
	CB	- 0.5	- 0.1	0.4	0.7**	- 0.1
Alkalinity	BC	- 2.81	- 0.11	0.06	0.14	-
	HP	- 0.19	0.01	0.21*	0.07	0.02
	CB	- 0.12	- 0.02	0.22*	- 0.00	- 0.01
pH	BC	- 0.06	0.04*	- 0.05	- 0.17*	0.02
	HP	- 0.06*	0.02	- 0.02	- 0.04	0.01
	CB	- 0.04	0.02	0.09*	- 0.04	0.02
Ca	BC	- 0.17*	0.01	0.11	- 0.04	0.01
	HP	- 0.04	- 0.02	0.06	0.04	- 0.01
	CB	- 0.04	- 0.01	- 0.06	0.08	0.02
Mg	BC	- 0.05*	0.00	- 0.04	0.01	- 0.00
	HP	- 0.05*	0.00	- 0.01	0.02*	- 0.00
	CB	0.02	- 0.00	0.02	0.02**	0.00
Na	BC	0.03	- 0.01	0.06	0.04**	- 0.01
	HP	0.02	- 0.02*	- 0.03	0.06	- 0.02
	CB	0.01	- 0.02*	0.09	0.05*	0.01
K	BC	- 0.003	0.002	0.01	0.01	- 0.0003
	HP	- 0.003	- 0.003	- 0.01	0.01	- 0.002
	CB	- 0.002	- 0.001	0.02	0.01	0.001
Cl	BC	- 0.03	0.004	0.01	0.03*	- 0.004
	HP	0.01	- 0.01	0.01	0.01	- 0.01*
	CB	- 0.03	- 0.0026	- 0.02	0.01	- 0.001
SO_4	BC	- 0.10	- 0.01	0.10	0.10	- 0.02
	HP	- 0.13	0.001	- 0.02	0.17	- 0.002
	CB	- 0.15	- 0.07	0.02	0.27*	- 0.08
DOC	BC	- 0.12	- 0.03	- 0.05	- 0.08	- 0.05
	HP	- 0.21	- 0.03	0.09	- 0.03	- 0.05
	CB	- 0.33*	- 0.05	0.16	0.24*	- 0.05
Colour	BC	- 0.4	0.3	1.0	- 2.3	- 0.3
	HP	0.2	- 0.8	2.4	2.0*	- 0.5
	CB	- 2.6	2.3	4.4	0.7	2.7
Al	BC	2.2	- 0.08	2.9	3.6	2.2
	HP	1.1	0.4	- 0.9	5.6	0.3
	CB	7.6	- 0.3	- 2.2	3.1	3.9

* $p < 0.05$
** $p < 0.01$

Table 5. Levels of significance of the results from the Lilliefors test of normality. Not significant (n.s.) indicates the data fit the normal distribution, and one or two stars indicate the Lilliefor's statistic exceeds the 0.95 or 0.99 quantile respectively.

Parameter	Blue Chalk	Harp	Chub
Annual			
Conductivity	**	**	**
Alkalinity	*	n.s.	**
pH	**	**	**
Ca	*	**	**
Mg	*	**	**
Na	**	**	**
K	**	**	**
Cl	**	**	**
SO_4	n.s.	**	**
DOC	n.s.	**	n.s.
Colour	n.s.	n.s.	n.s.
Al	**	**	**
Summer Stratified			
Conductivity	**	**	**
Alkalinity	n.s.	n.s.	n.s.
pH	**	*	**
Ca	*	*	*
Mg	**	*	**
Na	*	**	n.s.
K	**	**	n.s.
Cl	n.s.	**	*
SO_4	**	n.s.	**
DOC	**	**	n.s.
Colour	**	n.s.	**
Al	**	**	**
Ice Cover			
Conductivity	n.s.	*	n.s.
Alkalinity	n.s.	n.s.	n.s.
pH	n.s.	n.s.	n.s.
Ca	n.s.	n.s.	n.s.
Mg	n.s.	n.s.	n.s.
Na	n.s.	n.s.	n.s.
K	n.s.	n.s.	n.s.
Cl	**	n.s.	*
SO_4	n.s.	n.s.	n.s
DOC	n.s.	n.s.	n.s.
Colour	n.s.	n.s	n.s
Al	*	*	n.s

Table 6a. Comparison of Monte Carlo simulation with the parametric confidence limit for conductivity. L is the 97.5% interval about the mean assuming a normal distribution. Number of cases in the simulation above and below beyond the confidence interval were counted and expressed as a %. α is the probability of finding sample mean outside the 95% confidence interval.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	247	7.255	0	0.4	0.004
		2	30,381	5.130	0	0.8	0.008
		3	2,481,115	4.189	0	1.2	0.012
	SS	1	179	2.741	0.6	3.4	0.039
		2	15,931	1.938	1.1	3.3	0.045
		3	939,929	1.583	1.7	3.5	0.051
	IC	1	38	2.283	2.6	2.5	0.053
		2	703	1.614	3.7	5.0	0.087
		3	8,436	1.318	2.0	2.3	0.043
Harp	AN	1	244	3.559	0.8	1.6	0.025
		2	29,646	2.517	1.9	2.3	0.042
		3	2,391,444	2.055	2.4	2.4	0.048
	SS	1	176	8.352	0	0.6	0.006
		2	15,400	5.906	0	1.1	0.011
		3	893,200	4.822	0	1.7	0.017
	IC	1	42	3.550	0	4.8	0.048
		2	861	2.510	0.5	6.6	0.071
		3	11,480	2.050	0.7	5.4	0.061
Chub	AN	1	238	2.645	0.8	2.9	0.038
		2	28,203	1.870	1.1	3.4	0.045
		3	2,218,636	1.527	1.6	3.3	0.049
	SS	1	178	3.414	1.1	1.1	0.022
		2	15,753	2.414	2.3	1.8	0.041
		3	924,176	1.971	2.6	2.0	0.046
	IC	1	42	3.926	0	2.4	0.024
		2	861	2.776	1.5	3.2	0.047
		3	11,480	2.267	1.6	3.0	0.046

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 6b. Comparison of Monte Carlo simulation count of number of Monte Carlo cases beyond the 95% confidence limit (L) for alkalinity.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	120	0.748	1.7	1.7	0.033
		2	7,140	0.529	2.4	2.0	0.044
		3	280,840	0.432	2.5	2.2	0.047
	SS	1	87	0.799	2.3	2.3	0.046
		2	3,741	0.565	2.3	2.0	0.043
		3	105,995	0.461	2.4	2.2	0.046
	IC	1	19	0.358	0	0	0
		2	171	0.253	2.8	0	0.028
		3	969	0.207	2.9	0.4	0.032
Harp	AN	1	122	0.441	0.8	2.5	0.033
		2	7,381	0.312	0.9	3.4	0.043
		3	295,240	0.254	1.2	3.6	0.048
	SS	1	87	0.413	1.1	1.1	0.023
		2	3,741	0.292	1.0	2.6	0.036
		3	105,995	0.238	1.2	3.5	0.047
	IC	1	19	0.438	0	5.3	0.053
		2	171	0.310	2.2	4.2	0.064
		3	969	0.253	1.3	3.1	0.044
Chub	AN	1	116	0.416	0	4.3	0.043
		2	6,670	0.294	0.6	4.3	0.048
		3	253,460	0.240	0.8	4.3	0.051
	SS	1	84	0.421	0	3.6	0.036
		2	3,486	0.298	0.6	4.5	0.052
		3	95,284	0.243	0.7	4.8	0.055
	IC	1	20	0.409	0	5.0	0.050
		2	190	0.289	0	4.0	0.040
		3	1,140	0.239	1.0	3.1	0.041

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 6c. Comparison of Monte Carlo simulation with the parametric confidence limit. Number of cases in the simulation beyond the 95% confidence interval were counted for pH.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	238	0.393	4.2	0.8	0.050
		2	28,203	0.278	3.5	1.4	0.049
		3	2,218,636	0.227	3.4	1.5	0.050
	SS	1	179	0.387	4.5	1.1	0.056
		2	15,931	0.274	4.1	1.5	0.056
		3	939,929	0.224	4.0	1.5	0.054
	IC	1	38	0.288	5.3	0	0.053
		2	703	0.204	4.4	1.0	0.054
		3	8,436	0.166	3.9	1.3	0.052
Harp	AN	1	248	0.283	3.6	1.6	0.052
		2	30,628	0.200	2.9	2.8	0.057
		3	2,511,496	0.163	2.6	3.0	0.056
	SS	1	177	0.278	4.0	1.1	0.051
		2	15,576	0.196	3.7	2.4	0.062
		3	908,600	0.160	3.1	2.7	0.058
	IC	1	42	0.272	2.4	2.4	0.048
		2	861	0.192	2.3	2.9	0.053
		3	11,480	0.157	2.2	2.7	0.049
Chub	AN	1	244	0.351	0.8	4.1	0.049
		2	29,646	0.248	1.3	3.8	0.051
		3	2,391,444	0.203	1.5	3.5	0.049
	SS	1	179	0.392	0.6	3.9	0.045
		2	15,931	0.277	0.8	3.5	0.043
		3	939,929	0.226	0.9	3.8	0.047
	IC	1	42	0.358	0	2.4	0.024
		2	861	0.253	0.9	3.2	0.040
		3	11,480	0.207	1.6	2.8	0.044

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 6d. Comparison of Monte Carlo simulation with the parametric confidence limit. Number of cases in the simulation beyond the 95% confidence interval were counted for Ca.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	201	0.538	2.0	1.5	0.035
		2	20,100	0.380	2.0	2.9	0.049
		3	1,333,300	0.310	2.0	3.2	0.052
	SS	1	147	0.560	2.0	1.4	0.034
		2	10,731	0.396	2.2	3.1	0.053
		3	518,665	0.323	2.0	3.3	0.053
	IC	1	34	0.493	2.9	0	0.029
		2	561	0.349	1.1	3.4	0.045
		3	5,984	0.285	1.8	2.0	0.038
Harp	AN	1	196	0.510	2.6	1.5	0.041
		2	19,110	0.360	1.8	3.4	0.052
		3	1,235,780	0.294	1.8	2.8	0.046
	SS	1	135	0.484	2.2	2.2	0.044
		2	9,045	0.342	2.1	2.9	0.050
		3	400,995	0.279	2.1	2.6	0.047
	IC	1	33	0.605	0	6.1	0.061
		2	528	0.428	1.2	1.8	0.030
		3	5,456	0.350	1.6	3.4	0.050
Chub	AN	1	199	0.704	0.5	2.0	0.025
		2	19,701	0.498	1.0	3.0	0.040
		3	1,293,699	0.407	1.5	3.0	0.045
	SS	1	138	0.698	0.7	2.9	0.036
		2	9,453	0.494	1.0	3.1	0.041
		3	428,536	0.403	1.3	3.2	0.045
	IC	1	38	0.762	0	2.6	0.026
		2	703	0.539	1.7	1.6	0.033
		3	8,436	0.440	1.6	1.3	0.029

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 6e. Comparison of Monte Carlo simulation with the parametric confidence limit. Number of cases in the simulation beyond the 95% confidence interval were counted for Mg.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	200	0.155	2.5	3.5	0.060
		2	19,900	0.110	3.1	3.1	0.062
		3	1,313,400	0.090	3.0	2.7	0.057
	SS	1	146	0.158	2.1	4.1	0.062
		2	10,585	0.112	2.9	3.3	0.062
		3	508,080	0.091	2.7	2.9	0.056
	IC	1	34	0.131	2.9	2.9	0.059
		2	561	0.093	1.9	4.2	0.061
		3	5,984	0.076	2.0	3.4	0.055
Harp	AN	1	200	0.157	1.5	3.5	0.050
		2	19,900	0.111	2.1	2.9	0.050
		3	1,313,400	0.091	2.1	2.7	0.048
	SS	1	135	0.152	1.5	3.0	0.044
		2	9,045	0.108	1.9	2.8	0.047
		3	400,995	0.088	2.0	2.8	0.049
	IC	1	37	0.163	0	2.7	0.027
		2	666	0.115	2.0	2.8	0.048
		3	7,770	0.094	2.0	3.0	0.050
Chub	AN	1	197	0.146	2.5	1.5	0.041
		2	19,306	0.103	1.8	2.3	0.041
		3	1,254,890	0.084	2.1	2.6	0.046
	SS	1	135	0.152	2.2	2.2	0.044
		2	9,045	0.108	1.7	2.5	0.042
		3	400,995	0.088	2.1	2.6	0.047
	IC	1	39	0.141	2.6	0	0.026
		2	741	0.100	2.9	0.9	0.037
		3	9,139	0.081	2.3	1.4	0.037

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 6f. Comparison of Monte Carlo simulation with the parametric confidence limit. Number of cases in the simulation beyond the 95% confidence interval were counted for Na.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	201	0.236	1.5	2.5	0.040
		2	20,100	0.167	1.7	3.2	0.048
		3	1,333,300	0.136	1.7	3.4	0.051
	SS	1	148	0.230	2.0	2.7	0.047
		2	10,878	0.163	1.9	3.7	0.057
		3	529,396	0.133	1.9	3.4	0.052
	IC	1	33	0.226	0	3.0	0.030
		2	528	0.160	0.4	3.8	0.041
		3	5,456	0.131	1.2	3.4	0.045
Harp	AN	1	202	0.218	1.0	3.0	0.040
		2	20,301	0.154	1.6	2.9	0.044
		3	1,353,400	0.126	1.9	3.1	0.050
	SS	1	135	0.195	0.7	4.4	0.052
		2	9,045	0.138	0.9	4.3	0.051
		3	400,995	0.113	1.1	3.8	0.049
	IC	1	39	0.237	5.1	5.1	0.103
		2	741	0.167	1.8	1.8	0.037
		3	9,139	0.137	2.5	2.5	0.050
Chub	AN	1	202	0.243	0	5.0	0.050
		2	20,301	0.172	0.7	4.1	0.049
		3	1,353,400	0.141	1.0	3.8	0.048
	SS	1	138	0.212	0.7	4.3	0.051
		2	9,453	0.150	1.5	3.3	0.048
		3	428,536	0.122	1.7	3.1	0.047
	IC	1	41	0.309	0	7.3	0.073
		2	820	0.219	0	3.9	0.039
		3	10,660	0.179	0.1	3.2	0.033

[1] AN = annual; SS = summer stratification; IC = ice-covered

Table 6g. Comparison of Monte Carlo simulation with the parametric confidence limit. Number of cases in the simulation beyond the 95% confidence interval were counted for K.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	201	0.094	3.0	2.5	0.055
		2	20,100	0.067	3.1	3.3	0.064
		3	1,333,300	0.054	2.7	3.4	0.061
	SS	1	149	0.098	2.7	3.4	0.060
		2	11,026	0.069	3.1	3.9	0.070
		3	540,274	0.027	2.7	3.9	0.066
	IC	1	32	0.086	3.1	0	0.031
		2	496	0.061	3.6	1.6	0.052
		3	4,960	0.050	3.2	2.0	0.052
Harp	AN	1	201	0.105	3.0	3.5	0.065
		2	20,100	0.074	2.3	3.3	0.056
		3	1,333,300	0.061	2.1	3.7	0.058
	SS	1	135	0.097	3.7	1.5	0.052
		2	9,045	0.069	2.4	2.6	0.050
		3	400,995	0.056	2.0	3.1	0.051
	IC	1	39	0.129	2.6	2.6	0.051
		2	741	0.091	3.5	2.0	0.055
		3	9,139	0.074	3.3	1.5	0.048
Chub	AN	1	202	0.104	0.5	1.5	0.020
		2	20,301	0.074	1.6	3.6	0.052
		3	1,353,400	0.060	1.6	2.9	0.045
	SS	1	138	0.103	0.7	2.2	0.029
		2	9,453	0.073	1.2	3.1	0.043
		3	428,536	0.059	1.4	2.9	0.044
	IC	1	41	0.113	0	0	0
		2	820	0.080	2.4	1.5	0.039
		3	10,660	0.065	2.0	1.6	0.036

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 6h. Comparison of Monte Carlo simulation with the parametric confidence limit. Number of cases in the simulation beyond the 95% confidence interval were counted for Cl.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	204	0.128	2.5	2.0	0.044
		2	20,706	0.091	2.4	2.4	0.048
		3	1,394,204	0.074	2.3	2.4	0.048
	SS	1	149	0.118	3.4	0.7	0.040
		2	11,026	0.084	3.2	1.5	0.047
		3	540,274	0.068	3.0	2.1	0.051
	IC	1	36	0.182	0	5.6	0.056
		2	630	0.129	0	5.9	0.059
		3	7,140	0.105	0.4	4.3	0.047
Harp	AN	1	203	0.243	3.0	3.0	0.059
		2	20,503	0.172	2.7	2.7	0.054
		3	1,373,701	0.140	1.9	2.9	0.048
	SS	1	135	0.252	2.2	3.0	0.052
		2	9,045	0.178	1.3	3.1	0.044
		3	400,995	0.145	1.7	3.2	0.050
	IC	1	40	0.243	2.5	0	0.025
		2	780	0.172	4.3	1.5	0.057
		3	9,880	0.140	2.8	1.8	0.046
Chub	AN	1	201	0.239	1.0	2.5	0.035
		2	20,100	0.169	1.7	2.7	0.044
		3	1,333,300	0.138	2.0	2.8	0.048
	SS	1	138	0.230	1.5	2.9	0.044
		2	9,453	0.163	1.8	2.8	0.046
		3	428,536	0.403	1.3	3.2	0.045
	IC	1	42	0.298	0	2.4	0.024
		2	861	0.208	1.2	2.8	0.040
		3	11,480	0.170	1.3	3.1	0.045

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 6i. Comparison of Monte Carlo simulation with the parametric confidence limit. Number of cases in the simulation beyond the 95% confidence interval were counted for SO_4.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	199	1.261	0.5	2.0	0.025
		2	19,701	0.892	1.9	2.7	0.045
		3	1,293,699	0.728	2.1	2.7	0.048
	SS	1	148	1.276	0.7	2.0	0.027
		2	10,878	0.902	1.9	2.7	0.046
		3	529,396	0.737	2.1	2.7	0.048
	IC	1	32	1.049	0	0	0
		2	496	0.741	2.1	0.1	0.022
		3	4,960	0.605	2.5	2.4	0.048
Harp	AN	1	198	1.508	1.5	1.0	0.025
		2	19,503	1.066	1.3	2.8	0.041
		3	1,274,196	0.870	1.6	2.7	0.043
	SS	1	133	1.484	2.3	1.5	0.038
		2	8,778	1.050	1.5	3.1	0.046
		3	383,306	0.857	1.7	2.8	0.045
	IC	1	38	1.570	0	0	0
		2	703	1.110	1.3	3.4	0.047
		3	8,436	0.906	1.8	3.0	0.048
Chub	AN	1	200	2.131	0	2.5	0.025
		2	19,900	1.507	0.5	2.9	0.035
		3	1,313,400	1.230	1.4	2.9	0.042
	SS	1	136	2.090	0	2.2	0.022
		2	9,180	1.478	0.6	2.5	0.032
		3	410,040	1.207	1.4	2.9	0.043
	IC	1	42	2.300	0	0	0
		2	861	1.626	0.2	3.5	0.037
		3	11,480	1.328	1.7	2.4	0.040

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 6j. Comparison of Monte Carlo simulation with the parametric confidence limit. Number of cases in the simulation beyond the 95% confidence interval were counted for DOC.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	137	0.445	1.5	2.9	0.044
		2	9,316	0.315	2.0	3.6	0.056
		3	491,220	0.257	1.8	3.7	0.055
	SS	1	99	0.407	1.0	3.0	0.040
		2	4,851	0.288	1.0	3.5	0.045
		3	156,849	0.235	1.1	3.8	0.050
	IC	1	23	0.357	4.3	4.3	0.087
		2	253	0.252	1.5	3.4	0.049
		3	11,771	0.206	1.9	1.7	0.037
Harp	AN	1	144	1.678	1.4	4.2	0.056
		2	10,296	1.186	1.6	5.2	0.068
		3	487,344	0.969	1.3	6.5	0.078
	SS	1	96	1.739	1.0	5.2	0.063
		2	4,560	1.229	1.7	5.2	0.069
		3	142,880	1.004	1.6	6.7	0.083
	IC	1	26	0.668	3.8	0	0.038
		2	325	0.472	2.8	1.6	0.044
		3	2,600	0.385	1.9	2.6	0.045
Chub	AN	1	129	0.928	0	3.9	0.039
		2	8,256	0.656	1.0	2.9	0.039
		3	349,504	0.536	1.7	2.9	0.046
	SS	1	88	0.883	0	3.4	0.034
		2	3,828	0.624	0.5	3.4	0.039
		3	109,736	0.510	1.0	3.3	0.043
	IC	1	25	0.893	0	0	0
		2	300	0.631	3.5	0.6	0.042
		3	2,300	0.516	2.9	1.1	0.040

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 6k. Comparison of Monte Carlo simulation with the parametric confidence limit. Number of cases in the simulation beyond the 95% confidence interval were counted for colour.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	91	4.636	3.3	2.8	0.055
		2	4,095	3.278	2.5	2.2	0.047
		3	121,485	2.677	2.7	2.3	0.049
	SS	1	64	15.829	0	1.6	0.016
		2	2,016	11.192	0	3.1	0.031
		3	41,664	9.139	0	4.6	0.046
	IC	1	17	3.663	0	5.9	0.059
		2	136	2.590	3.5	3.1	0.066
		3	680	2.115	2.0	1.9	0.038
Harp	AN	1	95	8.743	5.3	3.2	0.084
		2	4,465	6.182	3.2	1.9	0.050
		3	138,415	5.048	3.0	2.0	0.049
	SS	1	65	8.244	6.2	0	0.062
		2	2,080	5.830	3.3	1.3	0.045
		3	43,680	4.760	3.2	1.4	0.046
	IC	1	17	6.771	0	5.9	0.059
		2	136	4.788	0.3	3.5	0.038
		3	680	3.909	0.4	3.9	0.043
Chub	AN	1	90	16.910	3.3	3.3	0.067
		2	4,005	11.957	2.9	2.5	0.054
		3	117,480	9.763	2.7	2.4	0.051
	SS	1	62	19.576	1.6	3.2	0.048
		2	1,891	13.843	1.6	3.7	0.053
		3	37,820	11.302	1.6	4.4	0.060
	IC	1	18	17.954	0	0	0
		2	153	12.696	0.9	0.9	0.019
		3	816	10.366	2.5	2.0	0.046

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 61. Comparison of Monte Carlo simulation count of number of Monte Carlo cases beyond the 95% confidence limit (L) for total aluminum.

Lake	Season[1]	Sample Size	Number of Cases	L	Monte Carlo %<($\bar{x}$-L)	Monte Carlo %>($\bar{x}$+L)	α
Blue Chalk	AN	1	94	21	0	8.5	0.085
		2	4,371	15	0	6.1	0.061
		3	134,044	12	0	4.6	0.046
	SS	1	63	16.33	0	6.3	0.063
		2	1,953	11.547	0	4.8	0.048
		3	39,711	9.428	0	4.3	0.043
	IC	1	19	25.434	0	5.3	0.053
		2	171	17.984	0	4.4	0.044
		3	969	14.684	0	4.6	0.046
Harp	AN	1	107	35	0.9	3.7	0.047
		2	5,671	25	0.4	4.6	0.050
		3	198,485	20	0.5	4.9	0.054
	SS	1	68	31.833	1.5	4.4	0.059
		2	2,278	22.509	0.7	5.1	0.058
		3	50,116	18.379	0.6	4.8	0.054
	IC	1	23	49.657	0	4.3	0.043
		2	253	35.113	0	8.1	0.081
		3	1,771	28.670	0	6.4	0.064
Chub	AN	1	111	52	1.8	4.5	0.063
		2	6,105	37	2.9	4.9	0.078
		3	221,815	30	2.8	4.0	0.068
	SS	1	73	47.584	1.4	4.1	0.055
		2	2,628	33.647	2.4	4.1	0.065
		3	62.196	27.472	2.8	3.5	0.062
	IC	1	24	51.42	4.2	0	0.042
		2	276	36.359	5.0	1.4	0.064
		3	1,932	29.687	4.2	1.4	0.056

[1] AN = annual; SS = summer stratification; IC = ice-covered.

Table 7. Estimated sampling frequency required of lake water chemistry parameters for various tolerances about the annual mean ($\bar{x}$), with 95% confidence, calculated using the standard error of multi-year data sets for Blue Chalk (BC), Harp (HP) and Chub (CB) Lakes. Quality control (QC) replicates are from Locke (1989).

		Required Sampling Frequency						
		QC Replicates for DRC Lakes					Distance from $\bar{x}$ with one sample	
Parameter	Lake	Analytical S.D.	Mean S.D.	Mean C.V.	10% of $\bar{x}$	20% of $\bar{x}$	Absolute	% of $\bar{x}$
Cond		0.22 µS	0.23 µS	1%				
	BC	145	132	78	1	1	2.65	9
	HP	98	89	38	1	1	2.18	6
	CB	263	240	144	1-2	1	3.57	12
Alk		0.05 mg/L	0.114 mg/L	15%				
	BC	209	40	2-3	3-4	1	0.72	18
	HP	78	15	1	1-2	1	0.44	14
	CB	69	13	16	35	9	0.42	59
pH		0.032 pH	0.039 pH	1%				
	BC	151	102	36	1	1	0.39	6
	HP	78	53	20	1	1	0.28	5
	CB	120	81	38	1	1	0.35	6
Ca		0.151 mg/L	0.076 mg/L	3%				
	BC	12-13	50	42	3-4	1	0.54	20
	HP	11-12	45	30	2-3	1	0.51	16
	CB	21-22	86	77	6-7	1- 2	0.70	26
Mg		0.042 mg/L	0.018 mg/L	2%				
	BC	13-14	74	109	4-5	1- 2	0.16	21
	HP	13-14	76	71	2-3	1	0.16	17
	CB	11-12	65	114	4-5	1- 2	0.15	21
Na		0.07 mg/L	0.026 mg/L	3%				
	BC	11-12	82	101	9-10	2- 3	0.24	30
	HP	9-10	70	53	4-5	1- 2	0.22	22
	CB	12	87	134	12-13	2- 3	0.24	35

Table 7. (Cont'd)

Parameter	Lake	Required Sampling Frequency: Analytical S.D.	QC Replicates for DRC Lakes: Mean S.D.	QC Replicates for DRC Lakes: Mean C.V.	10% of $\bar{x}$	20% of $\bar{x}$	Distance from $\bar{x}$ with one sample: Absolute	Distance from $\bar{x}$ with one sample: % of $\bar{x}$
K		0.04 mg/L	0.01 mg/L	2%				
	BC	6	96	175	6-7	1- 2	0.098	27
	HP	6	96	82	3-4	1	0.098	18
	CB	6	96	150	5-6	1- 2	0.098	25
Cl		0.051 mg/L	0.045 mg/L	11%				
	BC	6-7	8	7	8-9	2-3	0.13	30
	HP	20-21	26	7-8	9-10	2-3	0.23	30
	CB	21-22	28	20	23-24	6	0.24	49
SO_4		0.167 mg/L	0.141 mg/L	2%				
	BC	28	40	43	1-2	1	0.888	13
	HP	20	28	21	1	1	0.745	9
	CB	22	30	26	1-2	1	0.776	10
DOC		0.148 mg/L	0.115 mg/L	4%				
	BC	8-9	15-16	39	6-7	1-2	0.45	25
	HP	126	215	106	16-17	4-5	1.7	41
	CB	38	64	22	3-4	1	0.92	19
Colour		0.52 units	2.4 units	18%				
	BC	80	3-4	18-19	60	14-15	4.7	77
	HP	283	13-14	5-6	17-18	4-5	8.7	41
	CB	1,110	50	4-5	13-14	3-4	16.9	36
Al		5.3 mg/L	3.3 mg/L	8%				
	BC	16	41	519	333	83	21.2	182
	HP	32	84	76	49	12	30.0	70
	CB	97	250	46	30	7- 8	52.1	54

Table 8. Estimated sampling frequency required of lake water chemistry parameters for various tolerances about seasonal (summer stratified, SS; and ice cover, IC) mean ($\bar{x}$), with 95% confidence, calculated using the standard error of multi-year data sets for Blue Chalk (BC), Harp (HP) and Chub (CB) Lakes. Quality control (QC) replicates are from Locke 1989.

			Sampling Frequency						
			QC Replicates for DRC Lakes					Distance from $\bar{x}$ with one sample	
Parameter	Lake	Season	Analytical S.D.	Mean S.D.	Mean C.V.	10% of $\bar{x}$	20% of $\bar{x}$	Absolute	% of $\bar{x}$
Cond			0.22 µS	0.23 µS	1%				
	BC	SS	156	142	84	1	1	2.74	9
		IC	108	98	56	1	1	2.27	7
	HP	SS	46	42	17-18	1	1	1.49	4
		IC	260	238	98	1	1	3.55	10
	CB	SS	240	220	133	1-2	1	3.41	12
		IC	317	290	164	1-2	1	3.92	13
Alk			0.05 mg/L	0.114 mg/L	15%				
	BC	SS	234	45	1-2	3-4	1	0.764	19
		IC	51	9-10	1	1	1	0.359	9
	HP	SS	68	13	1	1-2	1	1.49	4
		IC	76	14-15	1	1-2	1	3.55	10
	CB	SS	74	14	16-17	38	9-10	0.431	62
		IC	74	14	16-17	37	9-10	0.429	61
pH			0.032 units	0.039 units	1%				
	BC	SS	147	99	35	1	1	0.388	6
		IC	81	55	20	1	1	0.288	5
	HP	SS	76	51	19-20	1	1	0.278	4
		IC	72	49	19	1	1	0.272	4
	CB	SS	124	83	39	1	1	0.357	6
		IC	126	85	41	1	1	0.359	6

Table 8. (Cont'd)

Parameter	Lake	Season	Sampling Frequency: QC Replicates for DRC Lakes: Analytical S.D.	Mean S.D.	Mean C.V.	10% of $\bar{x}$	20% of $\bar{x}$	Distance from $\bar{x}$ with one sample: Absolute	% of $\bar{x}$
K			0.04 mg/L	0.01 mg/L	2%				
	BC	SS	6	96	175	7-8	1-2	0.098	26
		IC	4-5	74	129	5-6	1-2	0.086	23
	HP	SS	4-5	74	66	2-3	1	0.086	16
		IC	10-11	167	138	5-6	1	0.129	24
	CB	SS	7-6	108	169	6-7	1-2	0.104	26
		IC	8-9	129	192	7-8	1-2	0.114	28
Cl			0.051 mg/L	0.045 mg/L	11%				
	BC	SS	5-6	6-7	6-7	7-8	1-2	0.118	28
		IC	8-9	11-12	8-9	10-11	1	0.151	33
	HP	SS	21	27	7-8	9-10	1	0.235	31
		IC	23	29	8-9	9-10	1	0.243	31
	CB	SS	20	26	18	22	1-2	0.229	47
		IC	25	33	21	25	1-2	0.257	50
SO_4			0.167 mg/L	0.141 mg/L	2%				
	BC	SS	31	43	47	1-2	2-3	0.929	14
		IC	19	27	28	1-2	1-2	0.733	11
	HP	SS	23	32	25	1	1	0.804	10
		IC	11-12	16-17	12-13	1	1-2	0.572	7
	CB	SS	21	30	26	1-2	2-3	0.770	10
		IC	25	35	29	1-2	4-5	0.829	11

Table 8. (Cont'd)

Parameter	Lake	Season	Sampling Frequency: QC Replicates for DRC Lakes: Analytical S.D.	Mean S.D.	Mean C.V.	10% of $\bar{x}$	20% of $\bar{x}$	Distance from $\bar{x}$ with one sample: Absolute	% of $\bar{x}$
Ca			0.151 mg/L	0.076 mg/L	3%				
	BC	SS	13-14	54	46	4-5	1-2	0.561	20
		IC	10-11	42	36	3-4	1	0.494	18
	HP	SS	10-11	41	27	2-3	1	0.484	16
		IC	16-17	64	40	3-4	1	0.606	19
	CB	SS	21	84	76	6-7	1-2	0.698	26
		IC	25	101	85	7-8	1-2	0.762	28
Mg			0.042 mg/L	0.018 mg/L	2%				
	BC	SS	14-15	78	115	4-5	1-2	0.159	21
		IC	9-10	53	77	3-4	1	0.131	18
	HP	SS	13-14	72	66	2-3	1	0.153	16
		IC	15-16	86	77	3-4	1	0.166	18
	CB	SS	13-14	72	126	5-6	1-2	0.153	22
		IC	11-12	61	102	4-5	1-2	0.141	20
Na			0.07 mg/L	0.026 mg/L	3%				
	BC	SS	10-11	78	99	8-9	2-3	0.229	30
		IC	10-11	75	82	7-8	1-2	0.225	27
	HP	SS	7-8	57	44	4	1	0.196	20
		IC	11-12	83	56	5-6	1-2	0.237	22
	CB	SS	9-10	66	108	9-10	2-3	0.212	31
		IC	19-20	142	185	16-17	4-5	0.310	41

Table 8. (Cont'd)

Parameter	Lake	Season	Sampling Frequency: QC Replicates for DRC Lakes: Analytical S.D.	Mean S.D.	Mean C.V.	10% of $\bar{x}$	20% of $\bar{x}$	Distance from $\bar{x}$ with one sample: Absolute	% of $\bar{x}$
DOC			0.115 mg/L	0.115 mg/L	4%				
	BC	SS	7-8	12-13	29	4-5	1-2	0.408	21
		IC	5-6	9-10	25	3-4	1	0.357	20
	HP	SS	138	229	113	17-18	4-5	1.74	42
		IC	20	34	10-11	2-3	1	0.668	16
	CB	SS	36	59	21	3-4	1	0.882	18
		IC	36	60	18-19	3-4	1	0.894	17
Colour			0.052 H units	2.4 H units	18%				
	BC	SS	53	2-3	6-7	31	7-8	3.80	56
		IC	50	2-3	8-9	101	25	3.67	100
	HP	SS	252	11-12	7-8	16-17	4-5	8.25	41
		IC	169	7-8	8-9	8-9	2-3	6.76	29
	CB	SS	912	43	18	12-13	3-4	15.7	35
		IC	1192	56	21	13-14	3-4	18.0	36
Al			5.3 mg/L	3.3 mg/L	8%				
	BC	SS	9-10	24	376	242	60	16.3	155
		IC	23	59	592	453	113	25.4	213
	HP	SS	36	93	87	56	13-14	31.8	75
		IC	28	77	82	52	13-14	28.9	72
	CB	SS	81	208	40	26	6-7	47.6	51
		IC	94	243	45	29	7-8	51.4	54

Fig. 4 Frequency distribution of 12 parameters identified in Table 2 in Blue Chalk Lake. The theoretical normal distribution about the mean is denoted by asterisks.

a. Conductivity	e. Mg	i. SO_4^-
b. Alkalinity	f. Na	j. DOC
c. pH	g. K	k. Colour
d. Ca	h. Cl	l. Al

Fig. 5 Frequency distribution of 12 parameters identified in Table 2 in Chub Lake. The theoretical normal distribution about the mean is denoted by asterisks.

a. Conductivity	e. Mg	i. SO_4^-
b. Alkalinity	f. Na	j. DOC
c. pH	g. K	k. Colour
d. Ca	h. Cl	l. Al

Fig. 6 Frequency distribution of 12 parameters identified in Table 2 in Harp Lake. The theoretical normal distribution about the mean is denoted by asterisks.

a. Conductivity	e. Mg	i. SO_4^-
b. Alkalinity	f. Na	j. DOC
c. pH	g. K	k. Colour
d. Ca	h. Cl	l. Al

Fig. 7 The distance from the mean value as a function of sample size (based on 95% confidence limits) for 12 parameters for each of 2 seasons for Blue Chalk, Chub and Harp Lakes.

a. Conductivity - SS	i. Mg - SS	q. SO_4^- - SS
b. Conductivity - IC	j. Mg - IC	r. SO_4^- - IC
c. Alkalinity - SS	k. Na - SS	s. DOC - SS
d. Alkalinity - IC	l. Na - IC	t. DOC - IC
e. pH - SS	m. K - SS	u. Colour - SS
f. pH - IC	n. K - IC	v Colour - IC
g. Ca - SS	o. Cl - SS	w. Al - SS
h. Ca - IC	p. CI - IC	x Al - IC

FIGURES

Fig. 1 Average concentrations of 12 key parameters identified in Table 2 in Blue Chalk Lake. Annual (AN) and seasonal (IF = ice-free, IC = ice-covered, FO = fall overturn, SS = summer stratified, SO = spring overturn) means are shown.

a. Conductivity
b. Alkalinity
c. pH
d. Ca
e. Mg
f. Na
g. K
h. Cl
i. SO_4^-
j. DOC
k. Colour
l. Al

Fig. 2 Average concentrations of 12 key parameters identified in Table 2 in Chub Lake. Annual (AN) and seasonal (IF = ice-free, IC = ice-covered, FO = fall overturn, SS = summer stratified, SO = spring overturn) means are shown.

a. Conductivity
b. Alkalinity
c. pH
d. Ca
e. Mg
f. Na
g. K
h. Cl
i. SO_4^-
j. DOC
k. Colour
l. Al

Fig. 3 Average concentrations of 12 key parameters identified in Table 2 in Harp Lake. Annual (AN) and seasonal (IF = ice-free, IC = ice-covered, FO = fall overturn, SS = summer stratified, SO = spring overturn) means are shown.

a. Conductivity
b. Alkalinity
c. pH
d. Ca
e. Mg
f. Na
g. K
h. Cl
i. SO_4^-
j. DOC
k. Colour
l. Al

Fig. 1.a

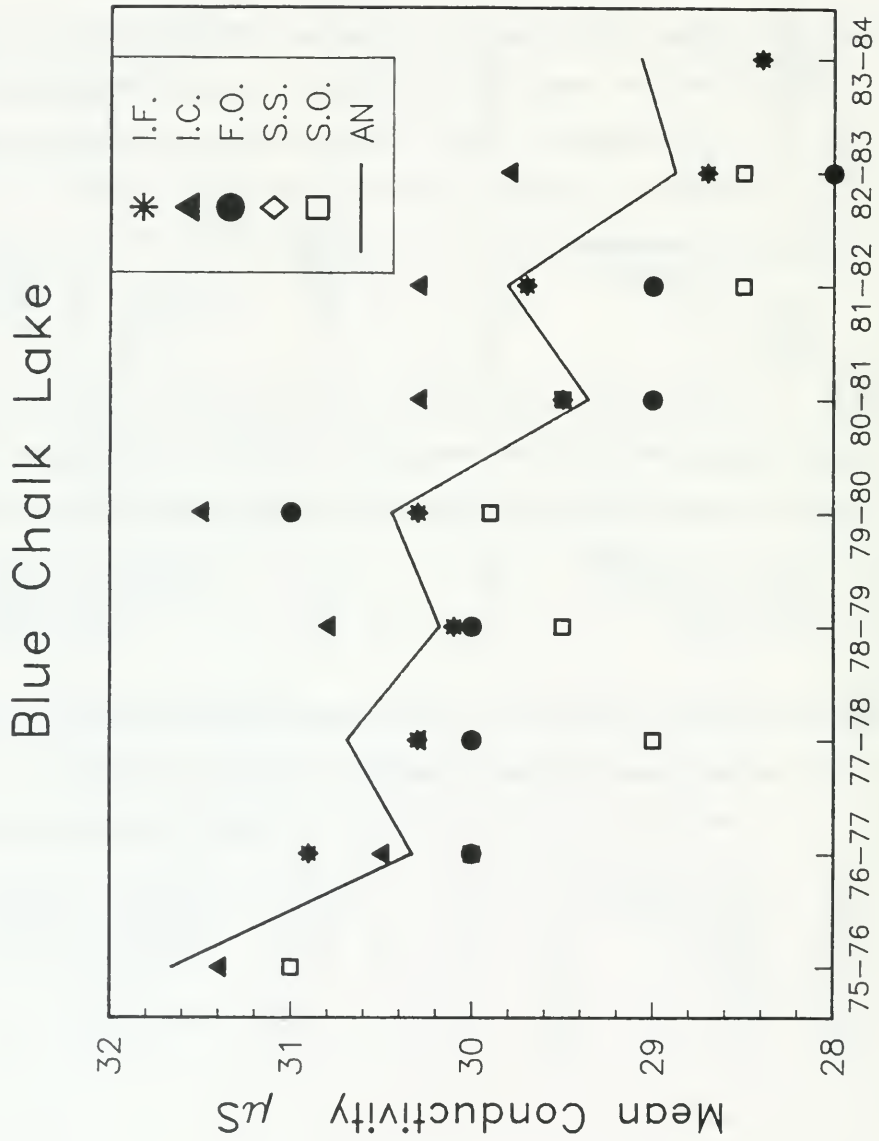

Blue Chalk Lake
Mean Conductivity μS
32
31
30
29
28
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84
Hydrologic Year
I.F.
I.C.
F.O.
S.S.
S.O.
AN

Fig. 1.b

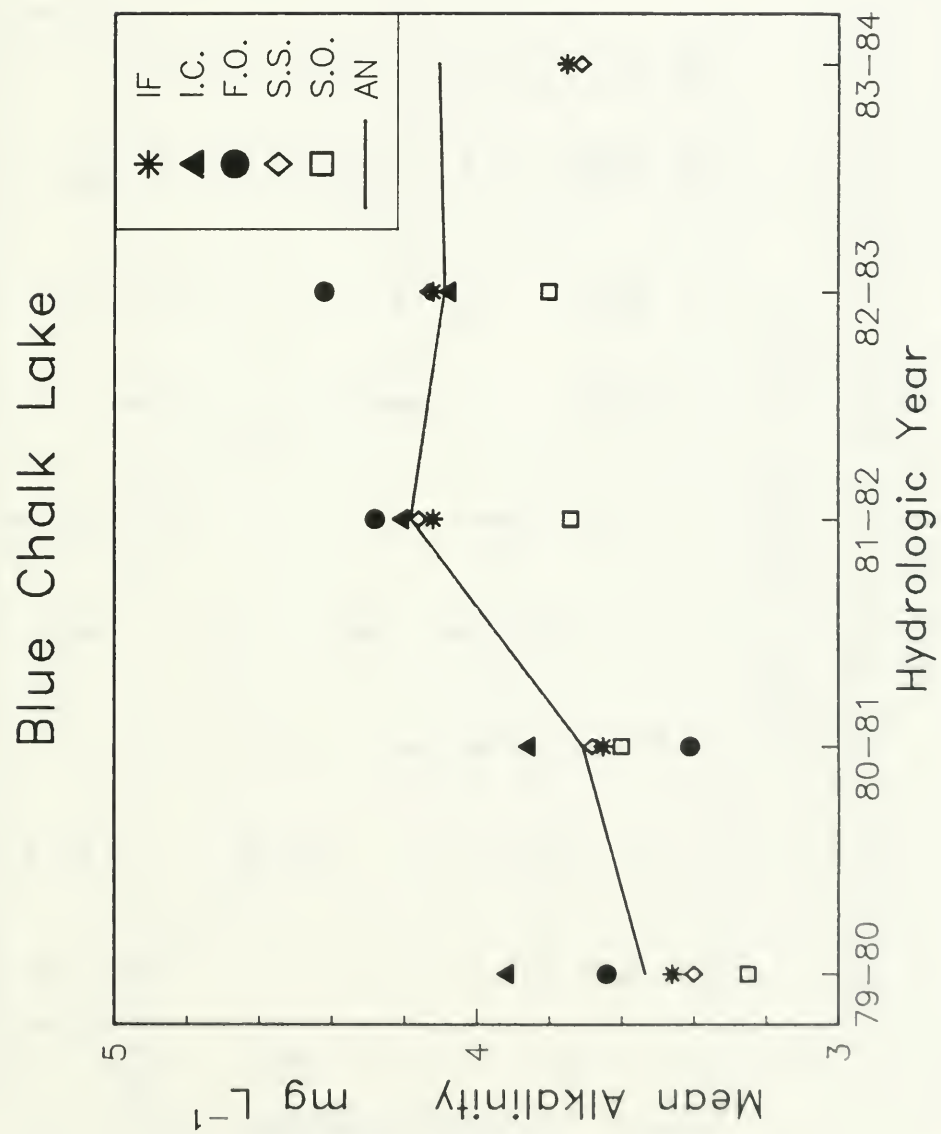

Blue Chalk Lake
Mean Alkalinity mg L⁻¹
5
4
3
79–80
80–81
81–82
82–83
83–84
Hydrologic Year
IF
I.C.
F.O.
S.S.
S.O.
AN

Fig. 1.c

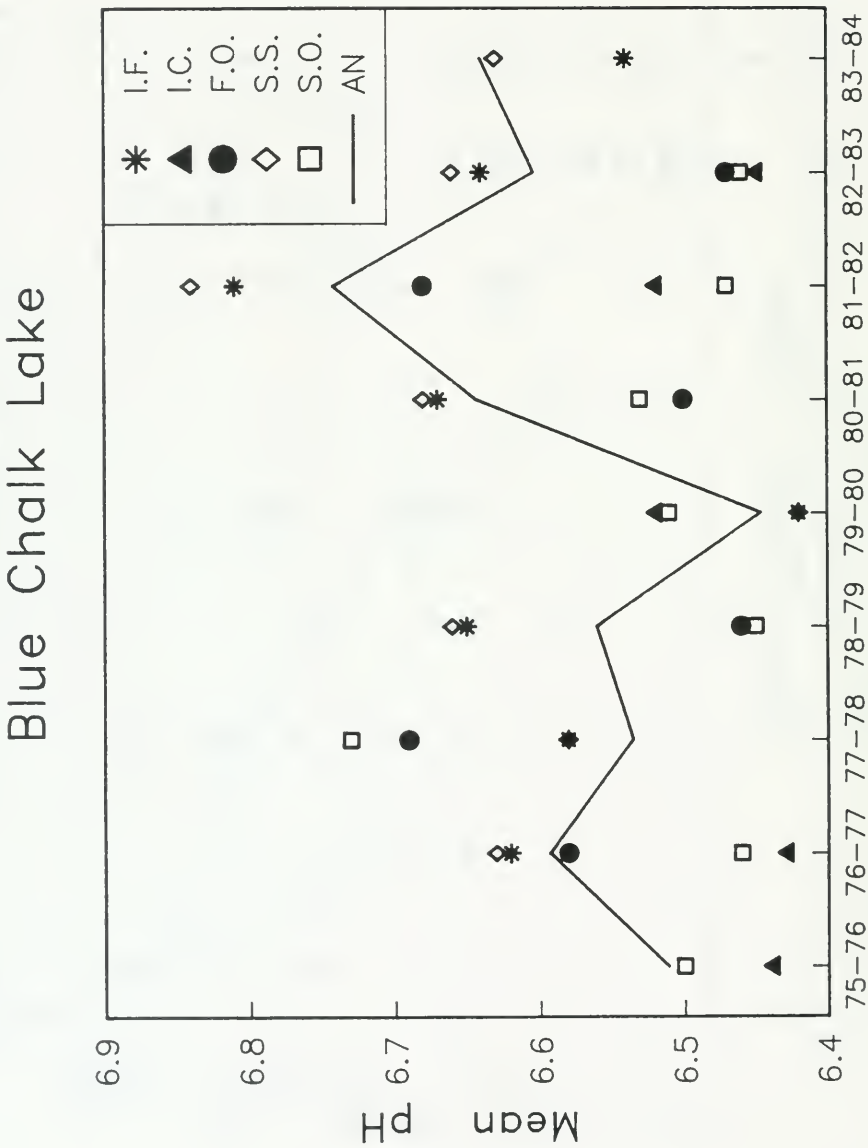

Blue Chalk Lake
Mean pH
6.9
6.8
6.7
6.6
6.5
6.4
75-76 76-77 77-78 78-79 79-80 80-81 81-82 82-83 83-84
Hydrologic Year
I.F.
I.C.
F.O.
S.S.
S.O.
AN

Fig. 1.d

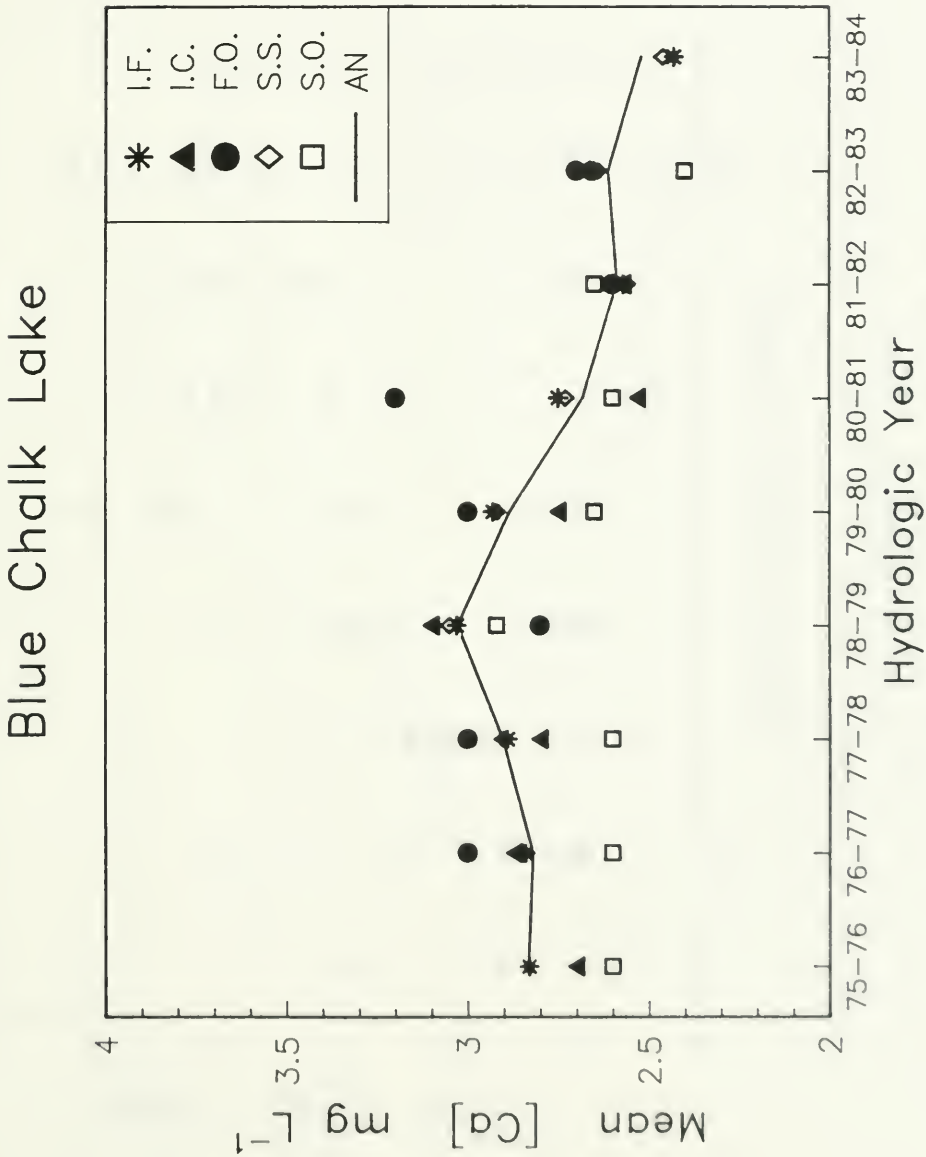

Blue Chalk Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [Ca] mg L⁻¹
4
3.5
3
2.5
2
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84
Hydrologic Year

Fig. 1.e

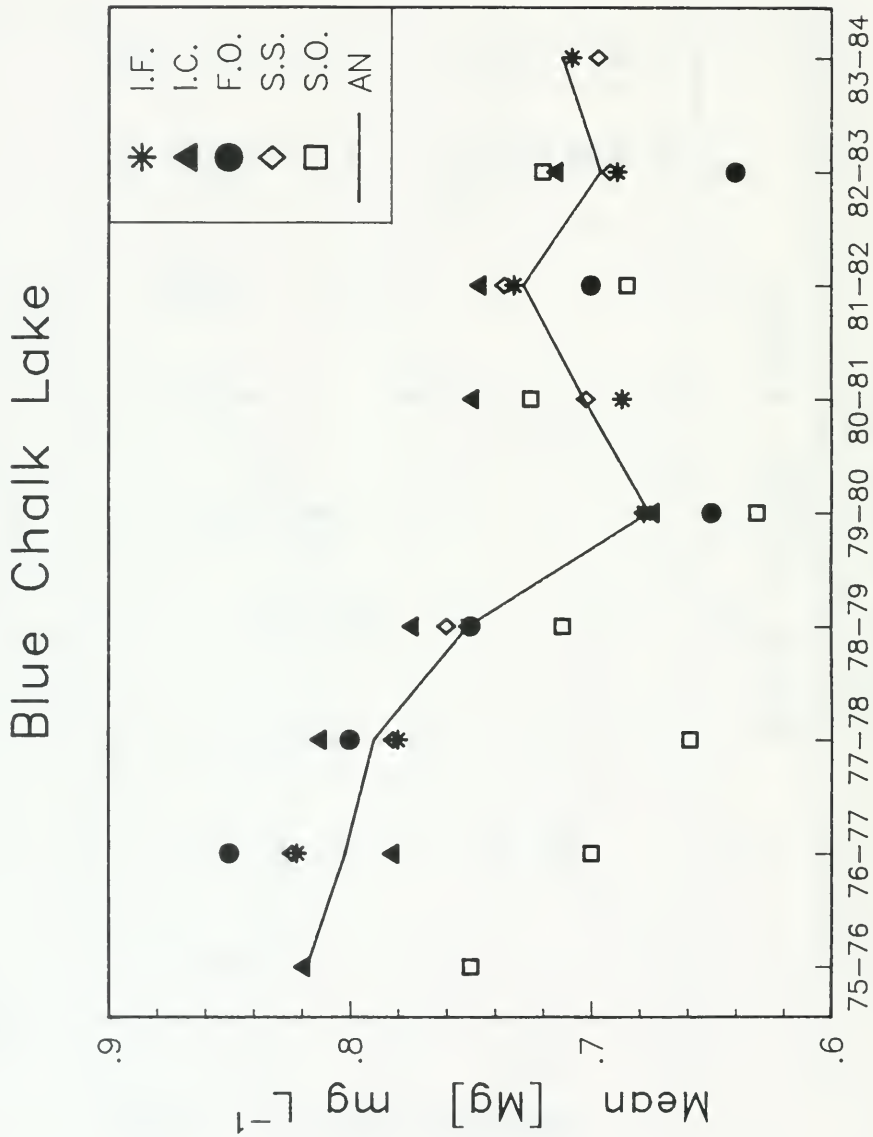

Blue Chalk Lake
Mean [Mg] mg L⁻¹
.9
.8
.7
.6
I.F.
I.C.
F.O.
S.S.
S.O.
AN
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84
Hydrologic Year

Fig. 1.f

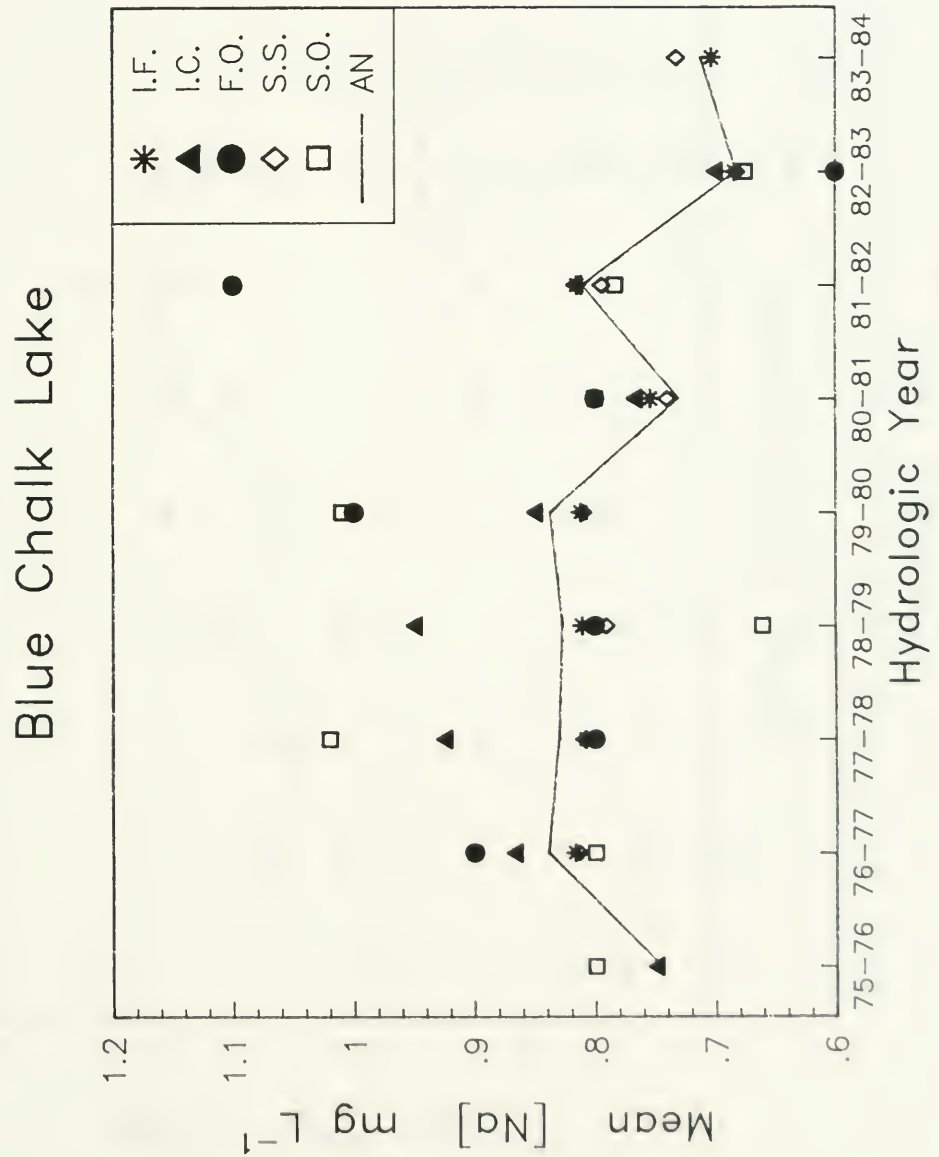
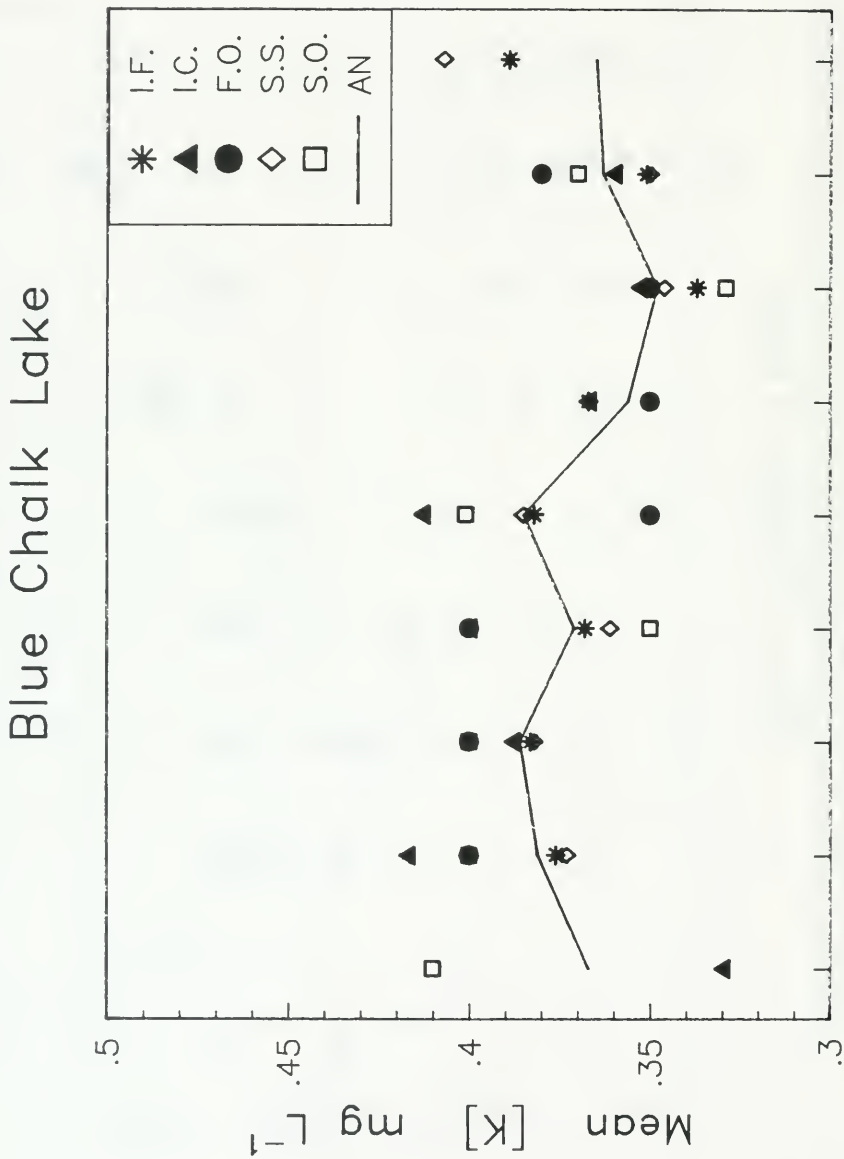

Blue Chalk Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [Na] mg L⁻¹
1.2
1.1
1
.9
.8
.7
.6
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84
Hydrologic Year

Fig. 1.g


Blue Chalk Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [K] mg L⁻¹
.5
.45
.4
.35
.3
75-76 76-77 77-78 78-79 79-80 80-81 81-82 82-83 83-84
Hydrologic Year

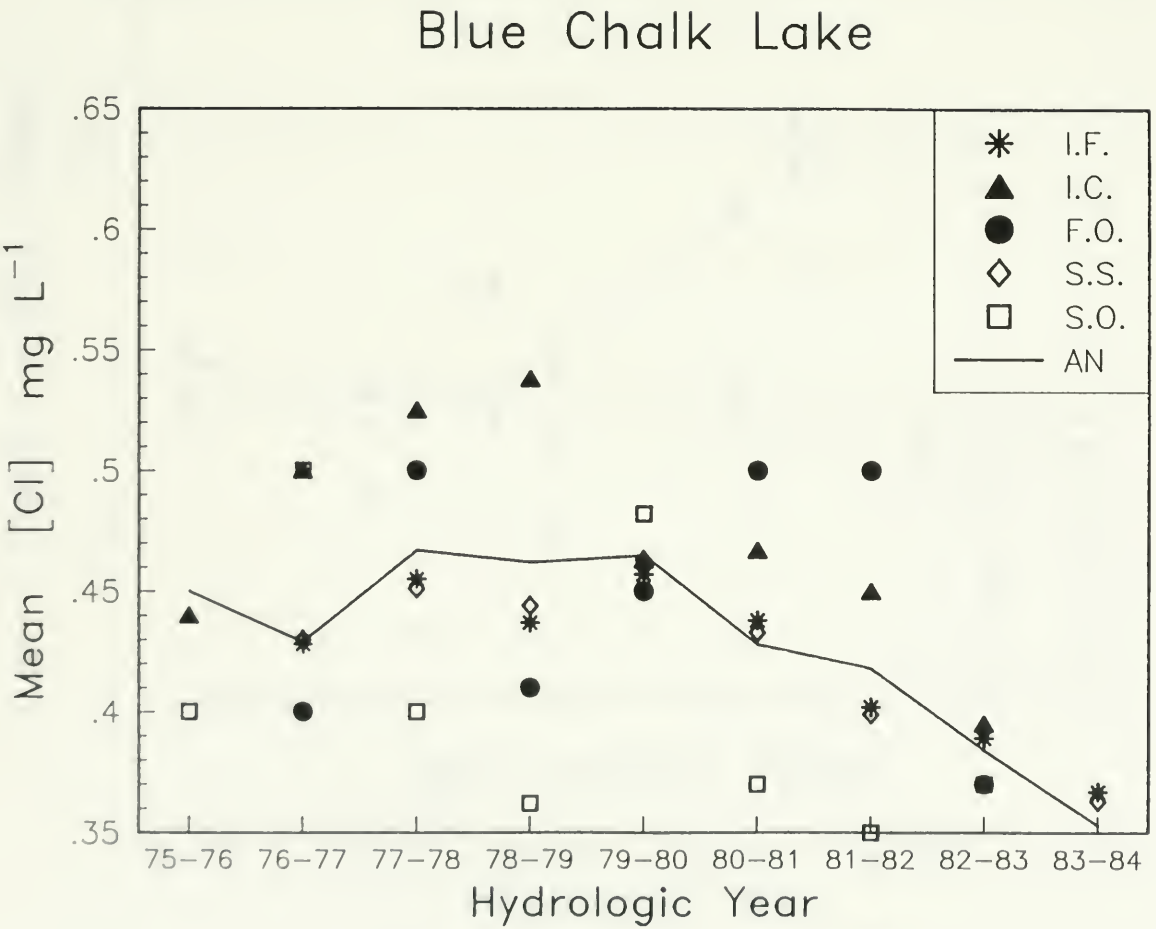

Blue Chalk Lake
.65
.6
.55
.5
.45
.4
.35
Mean [Cl] mg L^{-1}
I.F.
I.C.
F.O.
S.S.
S.O.
AN
75–76
76–77
77–78
78–79
79–80
80–81
81–82
82–83
83–84
Hydrologic Year

Fig. 1.h

Fig. 1.i

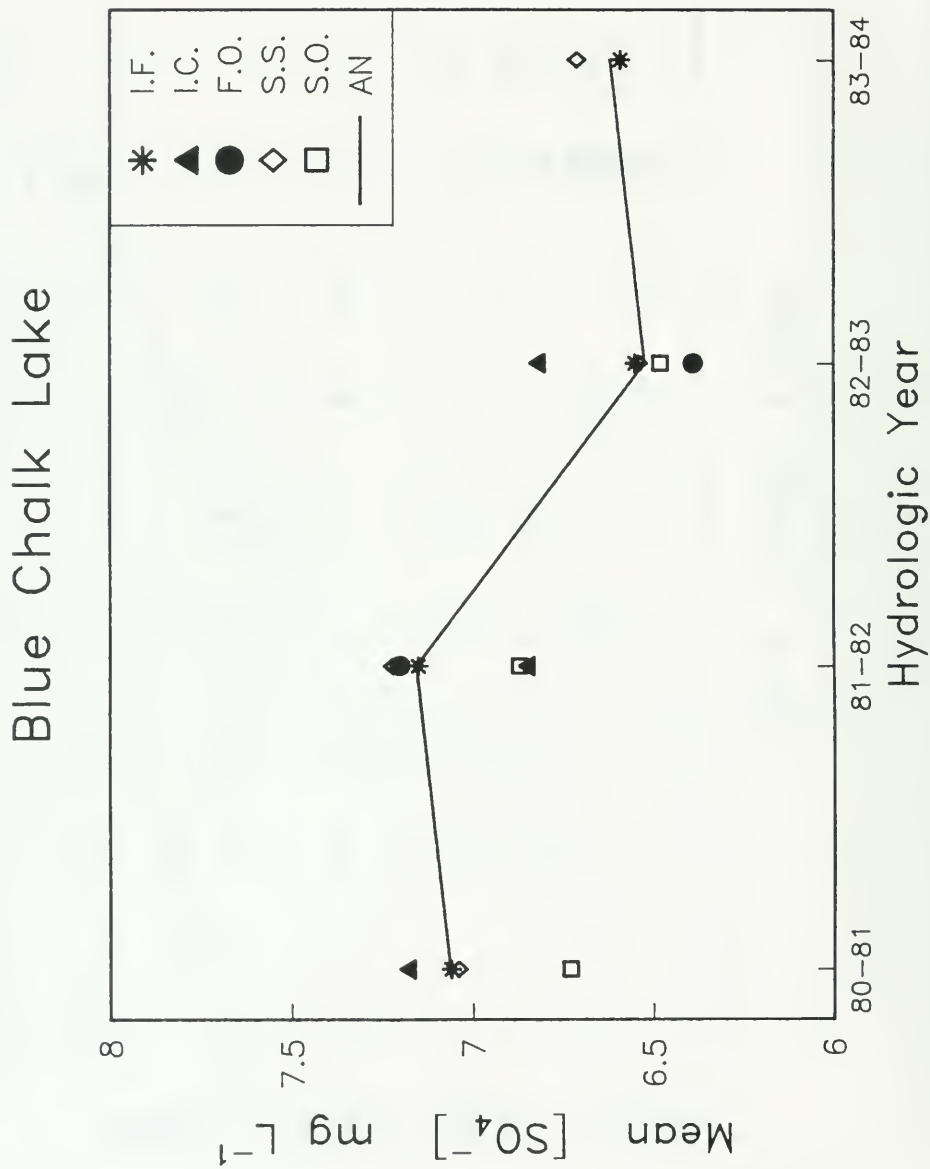

Blue Chalk Lake
Mean [SO4-] mg L-1
8
7.5
7
6.5
6
80-81
81-82
82-83
83-84
Hydrologic Year
I.F.
I.C.
F.O.
S.S.
S.O.
AN

Fig. 1.j

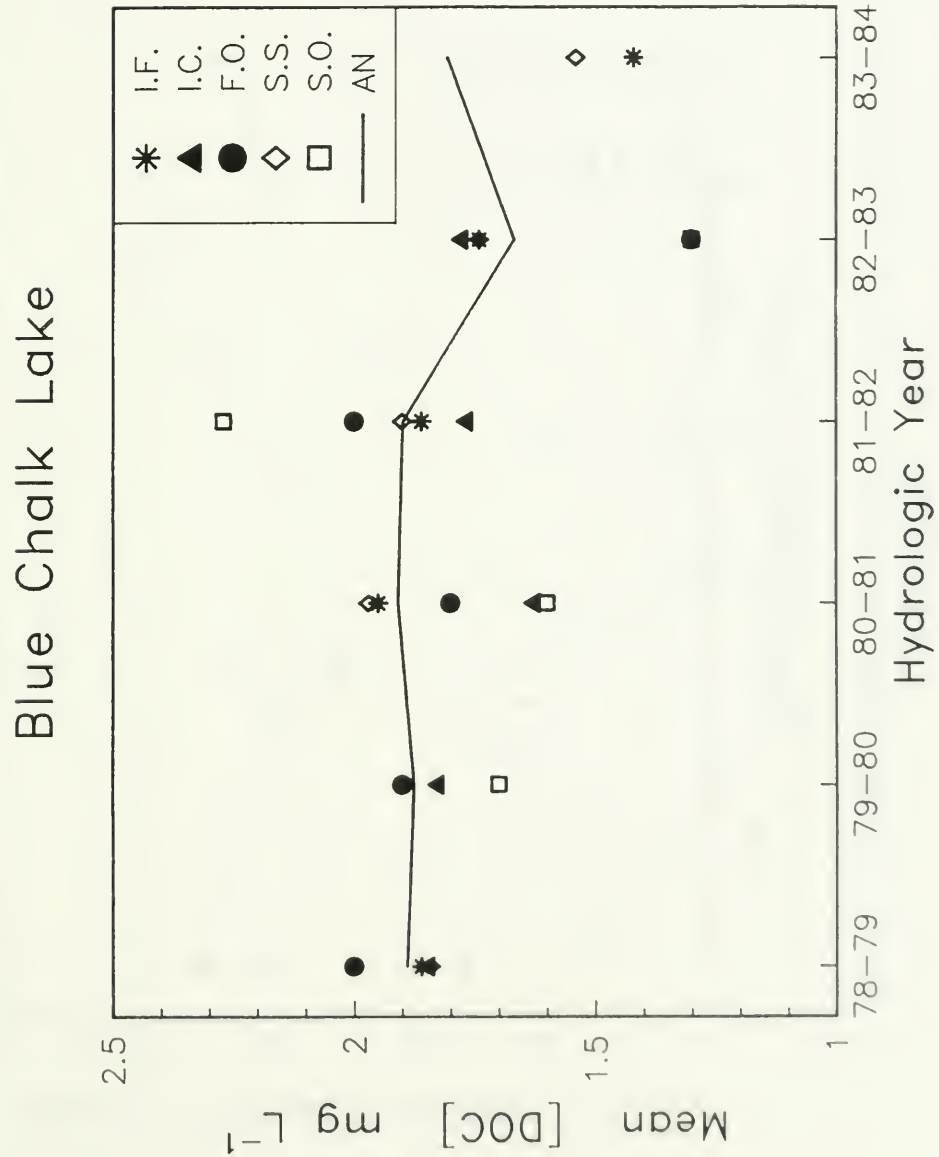

Blue Chalk Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [DOC] mg L⁻¹
2.5
2
1.5
1
78–79
79–80
80–81
81–82
82–83
83–84
Hydrologic Year

Fig. 1.k

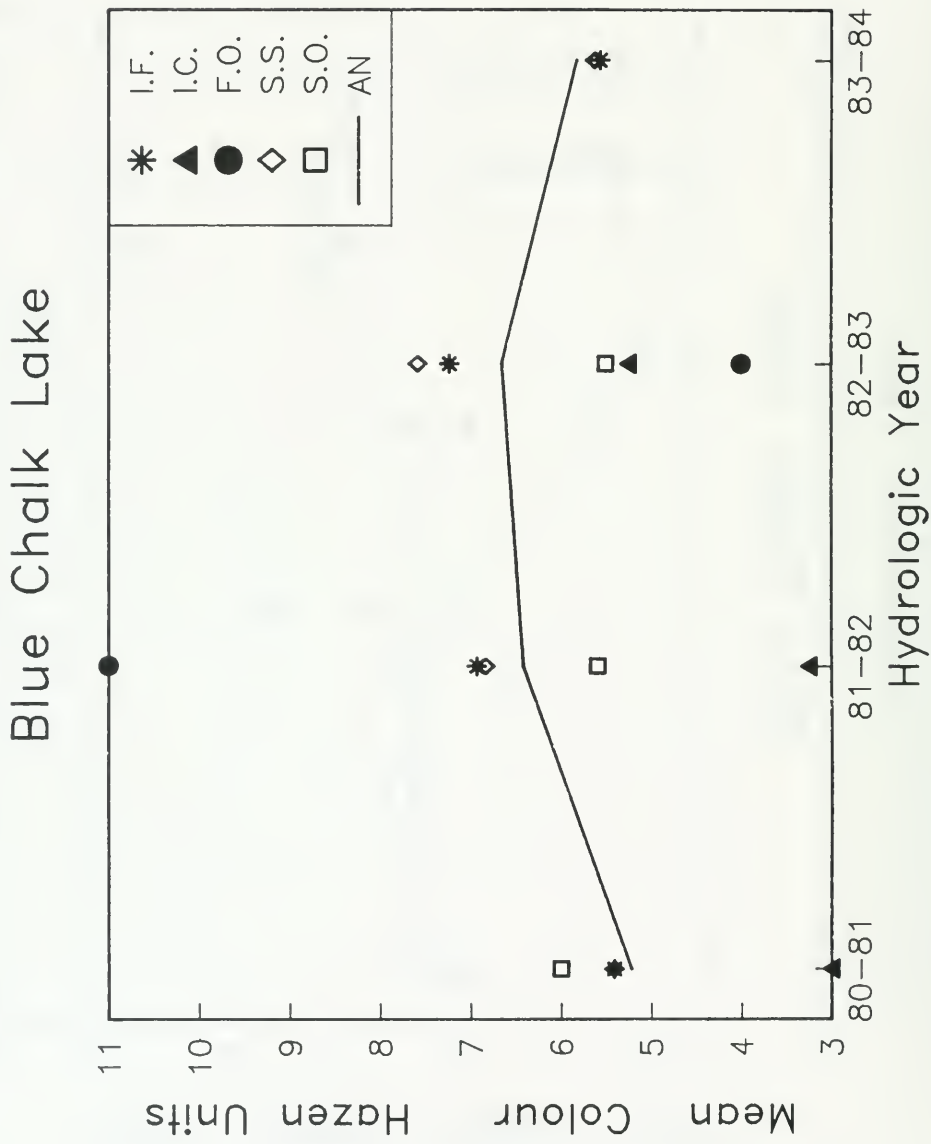

Blue Chalk Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean Colour Hazen Units
11
10
9
8
7
6
5
4
3
80–81
81–82
82–83
83–84
Hydrologic Year

Fig. 1.1

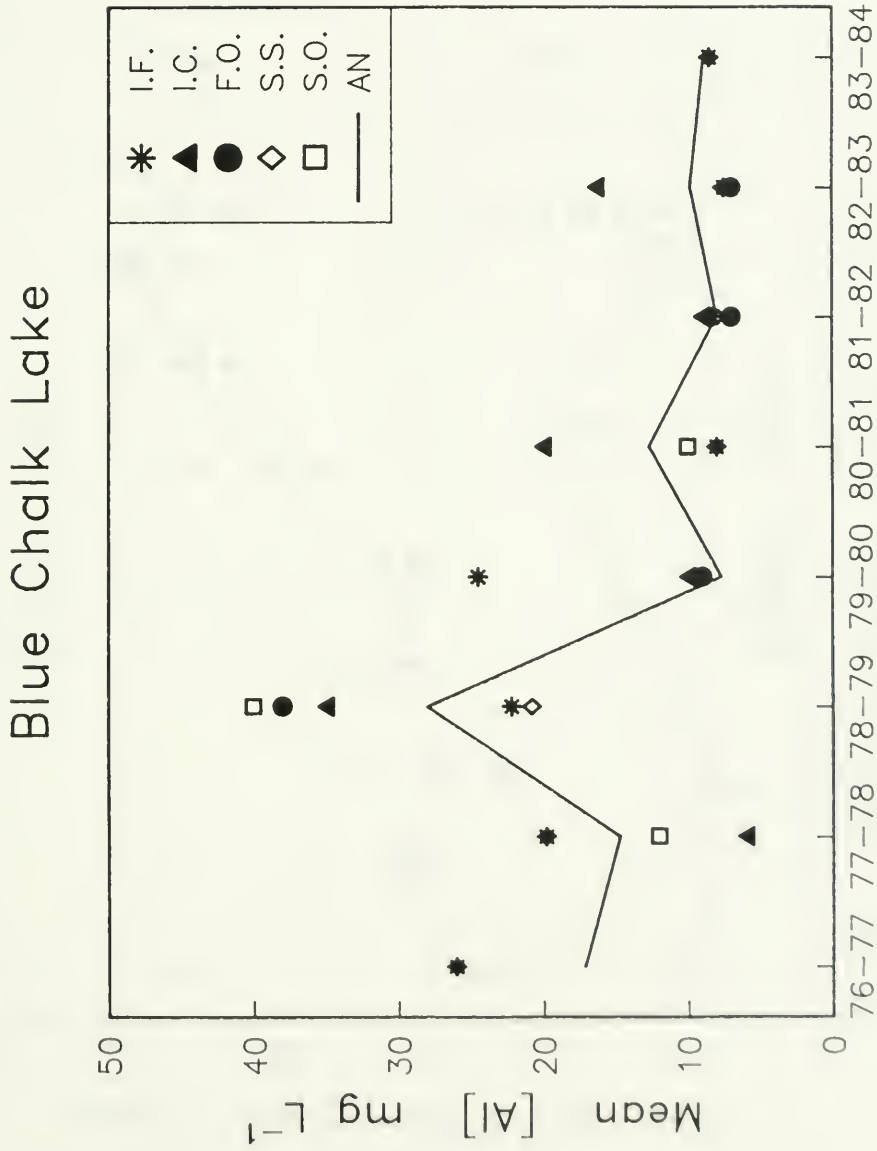

Blue Chalk Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [Al] mg L⁻¹
0
10
20
30
40
50
76–77
77–78
78–79
79–80
80–81
81–82
82–83
83–84
Hydrologic Year

Fig. 2.a

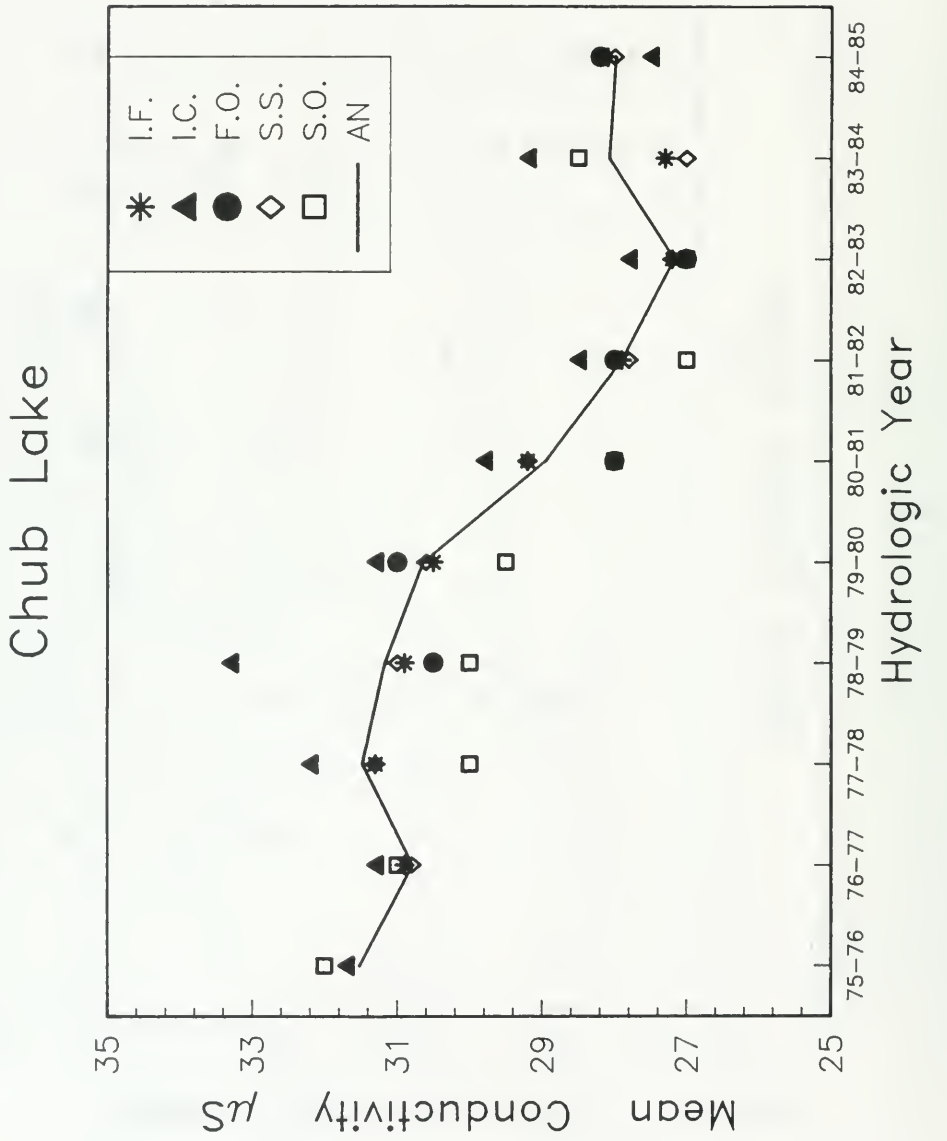

Chub Lake
Mean Conductivity μS
35
33
31
29
27
25
I.F.
I.C.
F.O.
S.S.
S.O.
AN
75–76
76–77
77–78
78–79
79–80
80–81
81–82
82–83
83–84
84–85
Hydrologic Year

Fig. 2.b

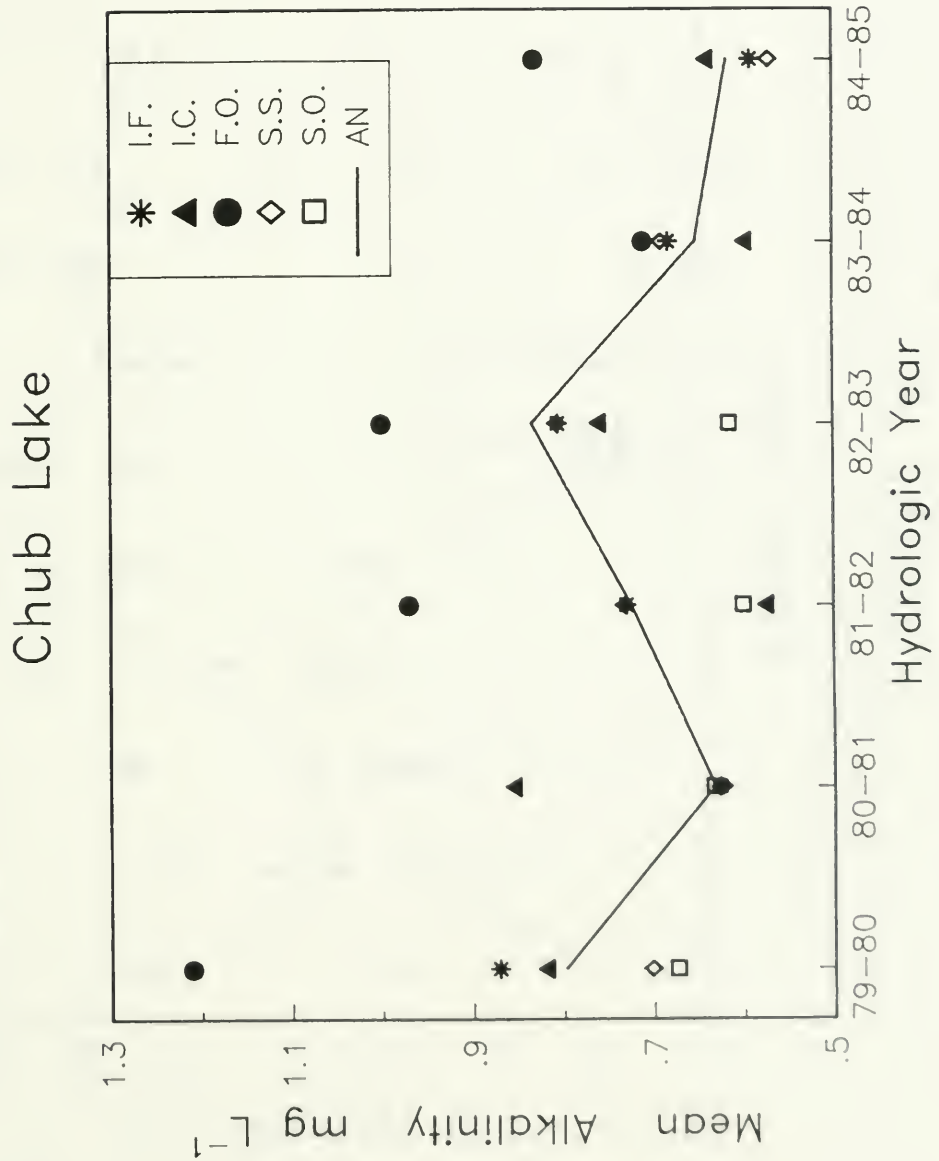

Chub Lake
Mean Alkalinity mg L⁻¹
1.3
1.1
.9
.7
.5
I.F.
I.C.
F.O.
S.S.
S.O.
AN
79–80
80–81
81–82
82–83
83–84
84–85
Hydrologic Year

Fig. 2.c

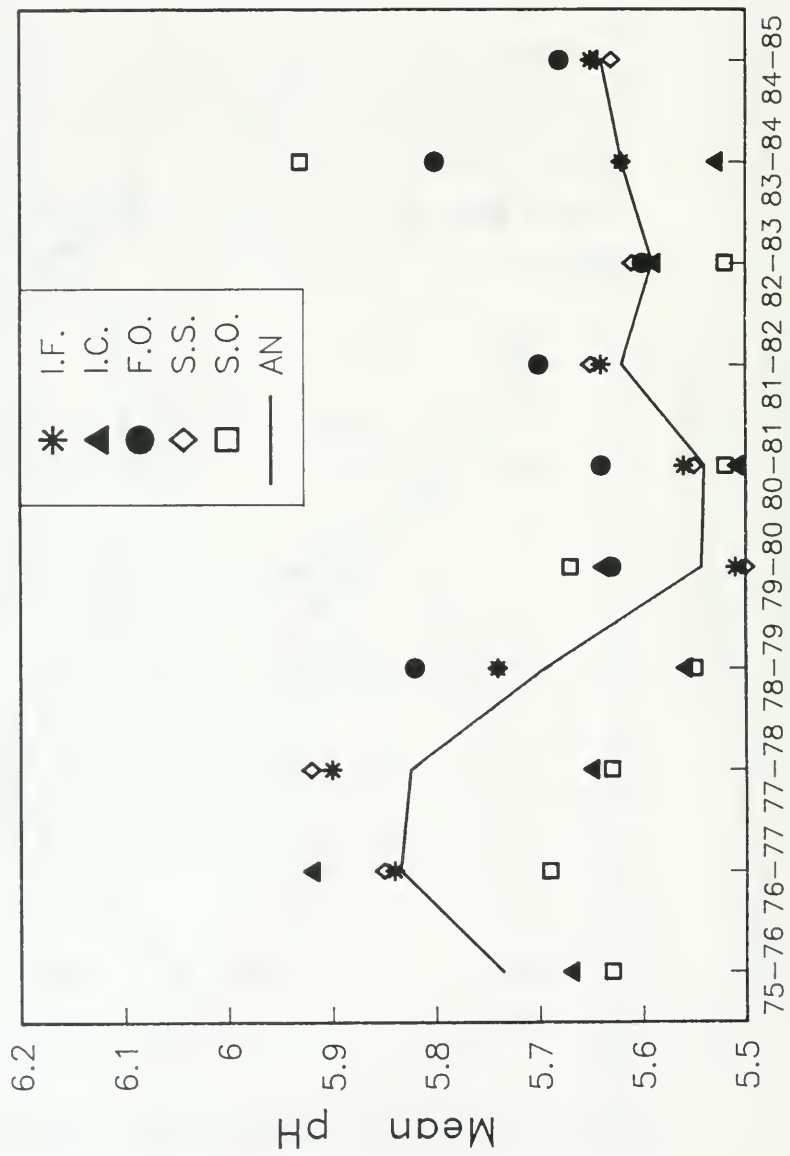

Chub Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean pH
6.2
6.1
6
5.9
5.8
5.7
5.6
5.5
75-76 76-77 77-78 78-79 79-80 80-81 81-82 82-83 83-84 84-85
Hydrologic Year

Fig. 2.d

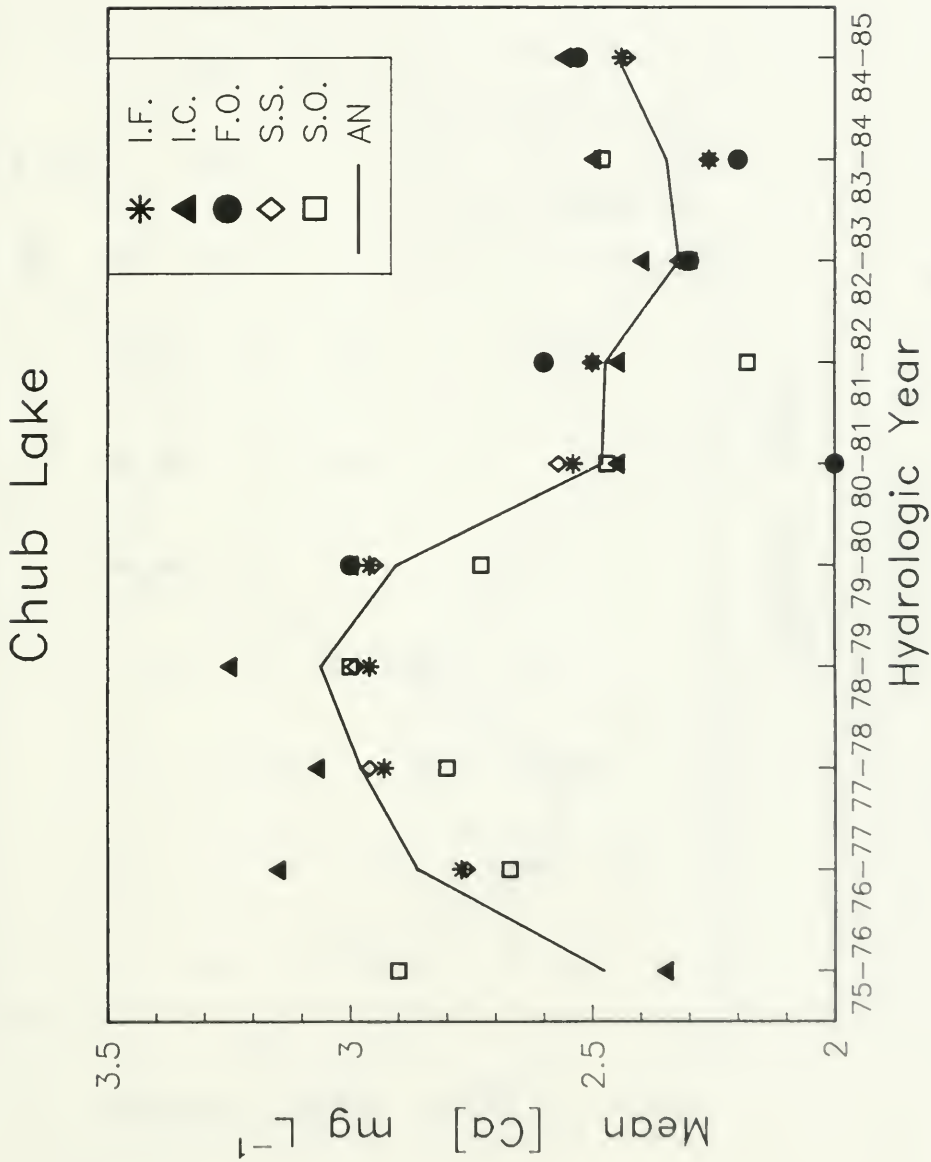

Chub Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [Ca] mg L⁻¹
3.5
3
2.5
2
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 2.e

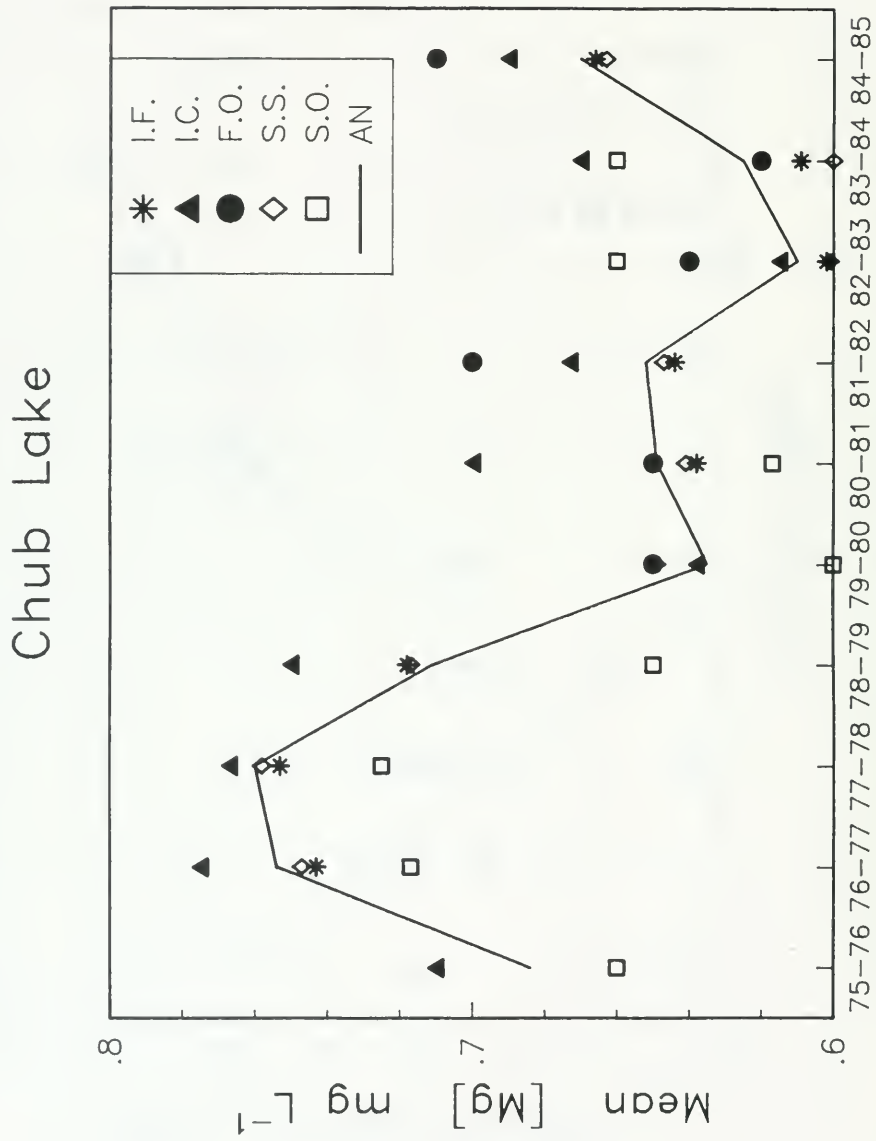

Chub Lake
Mean [Mg] mg L⁻¹
.8
.7
.6
I.F.
I.C.
F.O.
S.S.
S.O.
AN
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 2.f

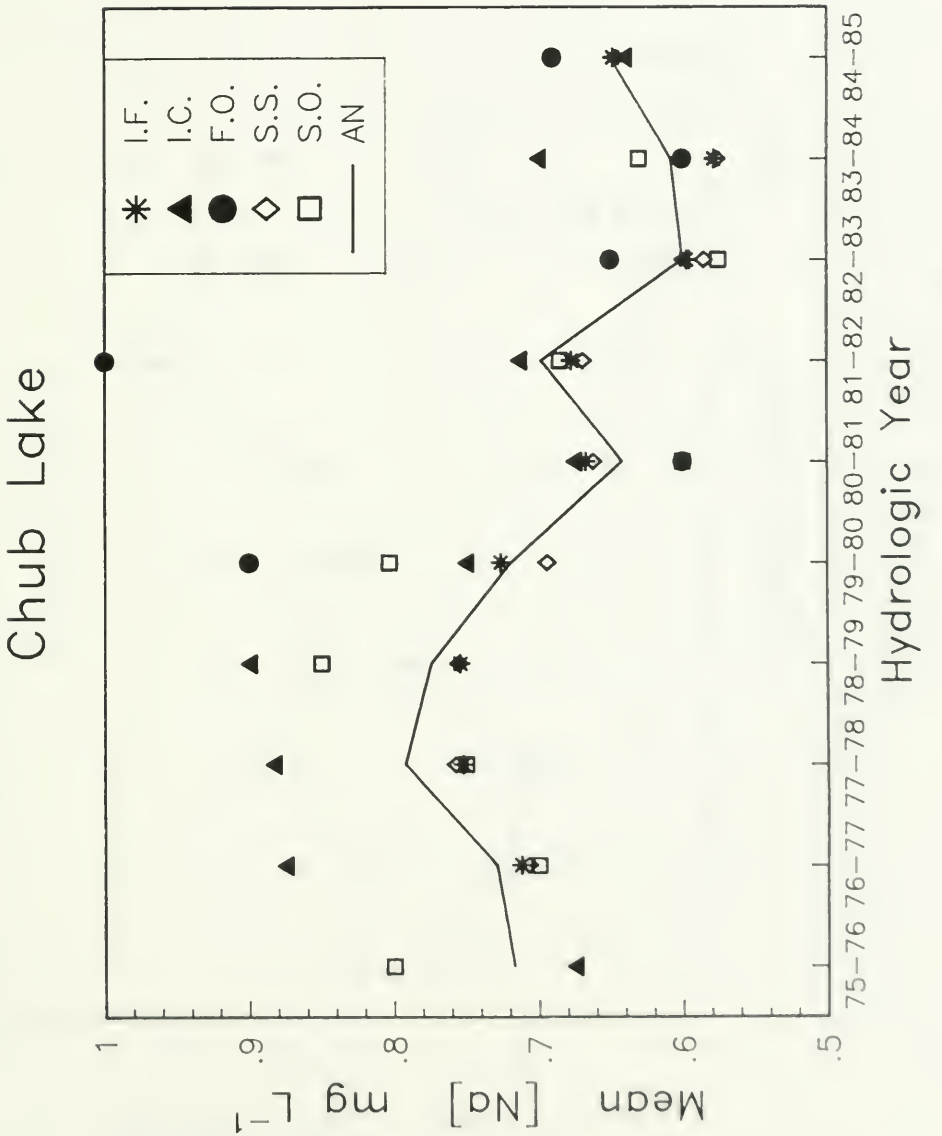

Chub Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [Na] mg L⁻¹
1
.9
.8
.7
.6
.5
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 2.g

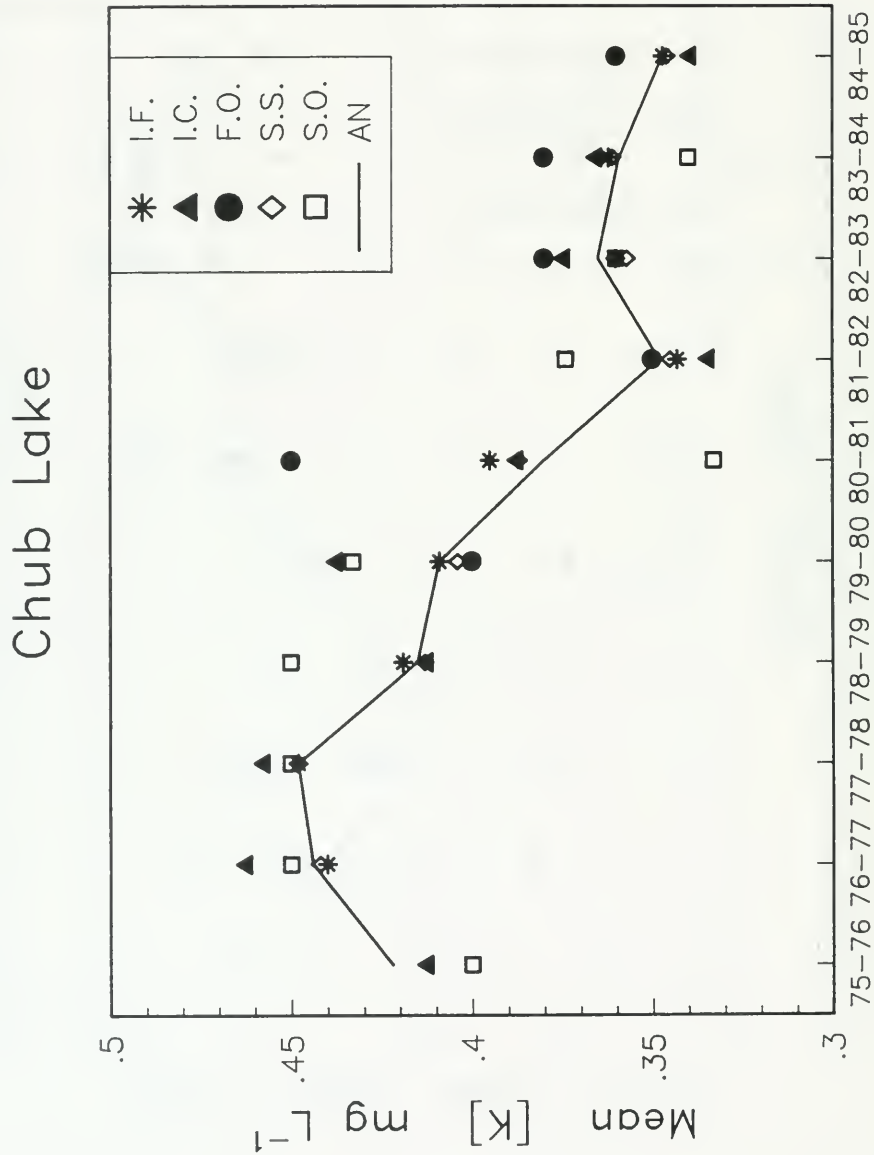

Chub Lake
Mean [K] mg L⁻¹
.5
.45
.4
.35
.3
I.F.
I.C.
F.O.
S.S.
S.O.
AN
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 2.h

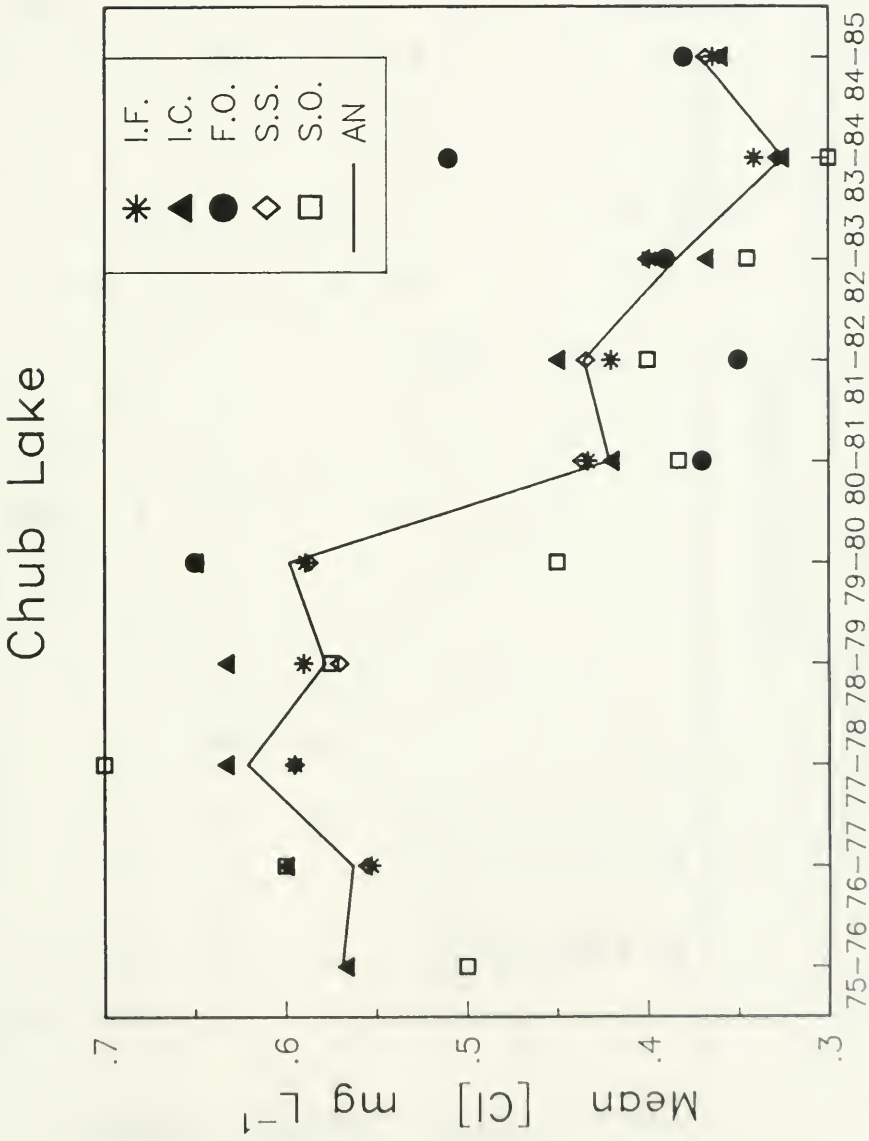

Chub Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [Cl] mg L⁻¹
.7
.6
.5
.4
.3
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 2.i

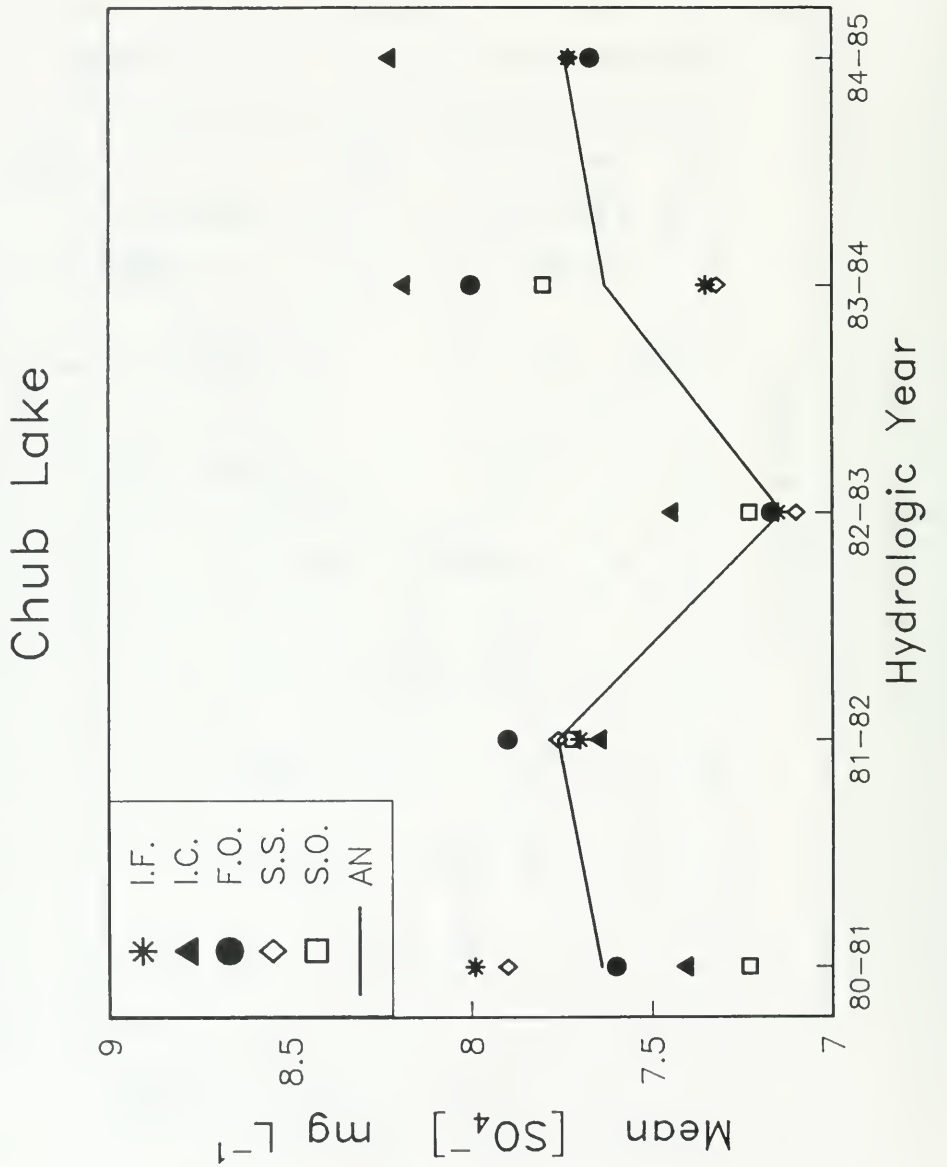

Chub Lake
Mean [SO4--] mg L-1
9
8.5
8
7.5
7
80-81
81-82
82-83
83-84
84-85
Hydrologic Year
I.F.
I.C.
F.O.
S.S.
S.O.
AN

Fig. 2.j

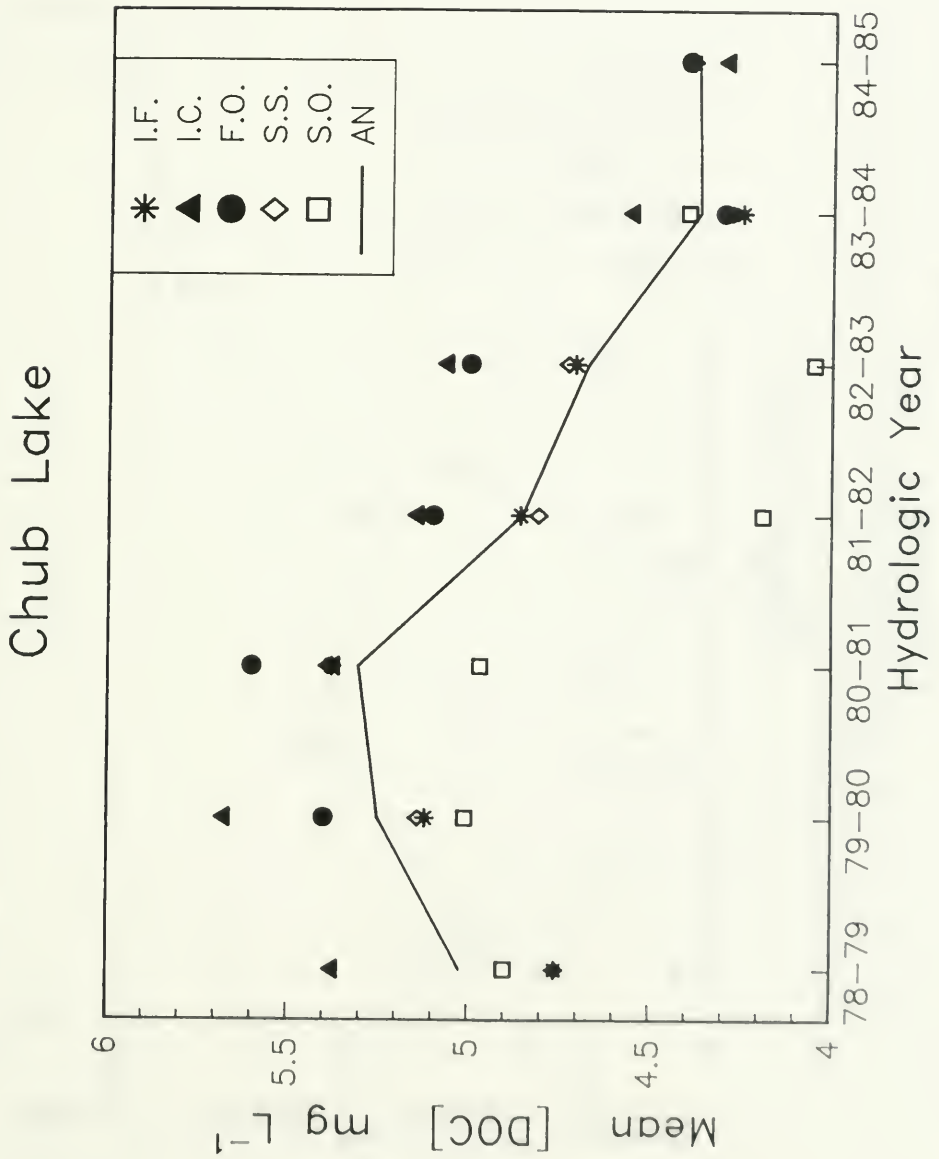

Chub Lake
Mean [DOC] mg L⁻¹
6
5.5
5
4.5
4
78–79
79–80
80–81
81–82
82–83
83–84
84–85
Hydrologic Year
I.F.
I.C.
F.O.
S.S.
S.O.
AN

Fig. 2.k

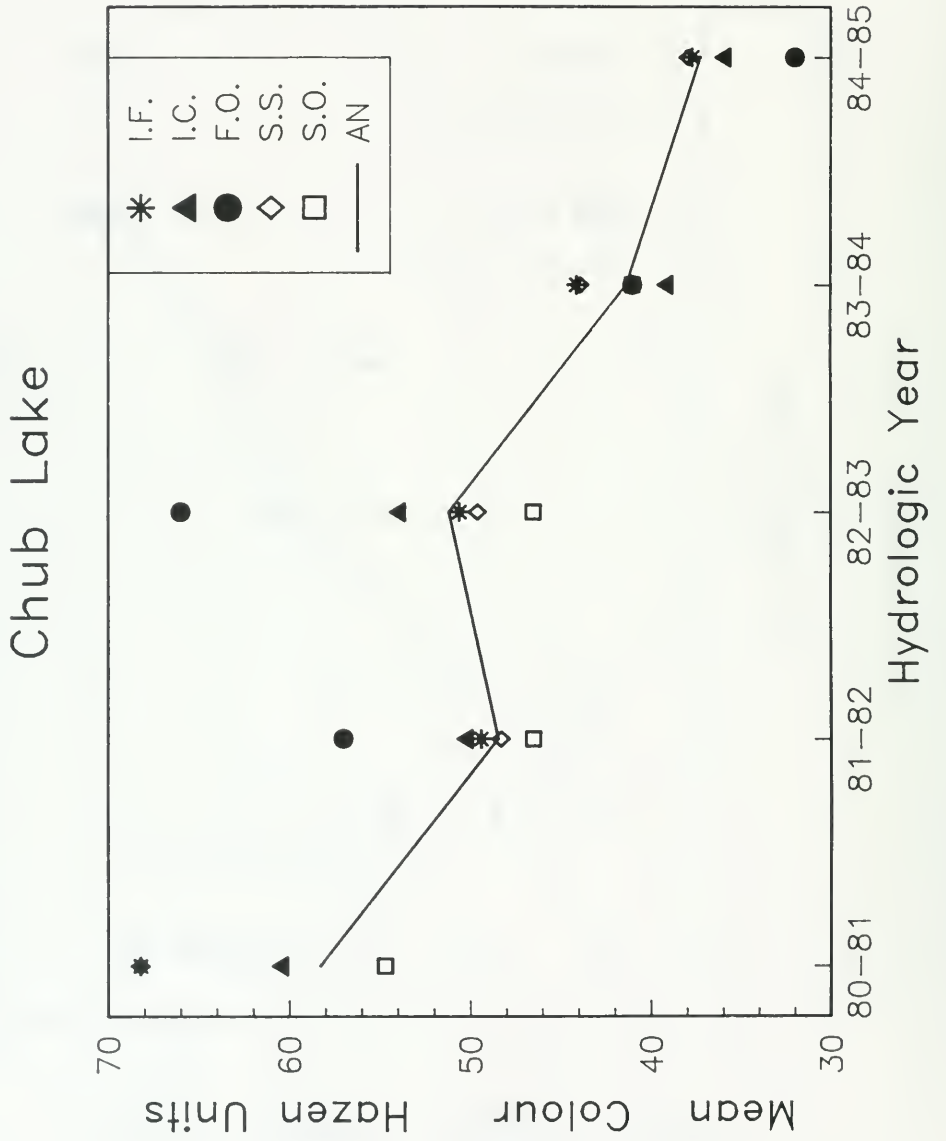

Chub Lake
Mean Colour Hazen Units
70
60
50
40
30
80–81
81–82
82–83
83–84
84–85
Hydrologic Year
I.F.
I.C.
F.O.
S.S.
S.O.
AN

Fig. 2.1

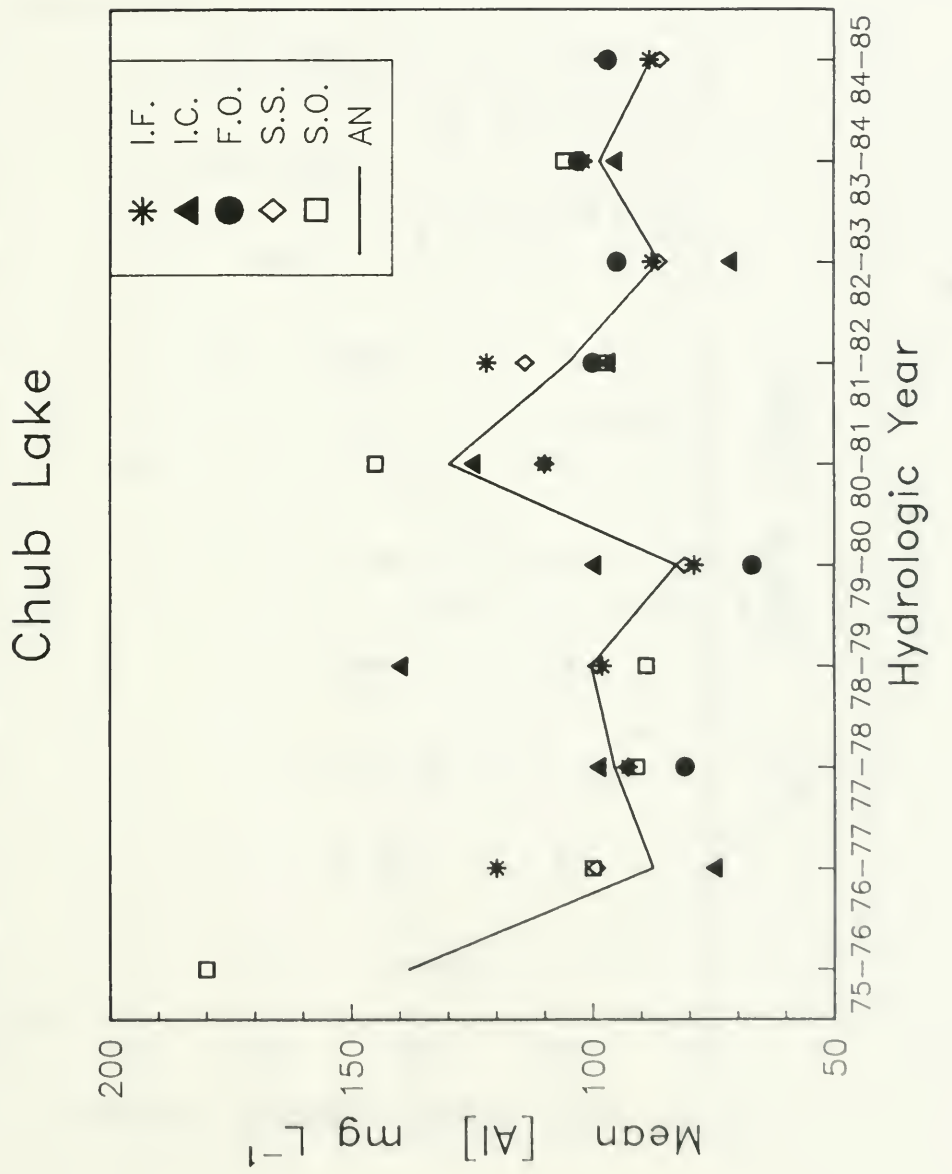

Chub Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [Al] mg L⁻¹
200
150
100
50
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 3.a

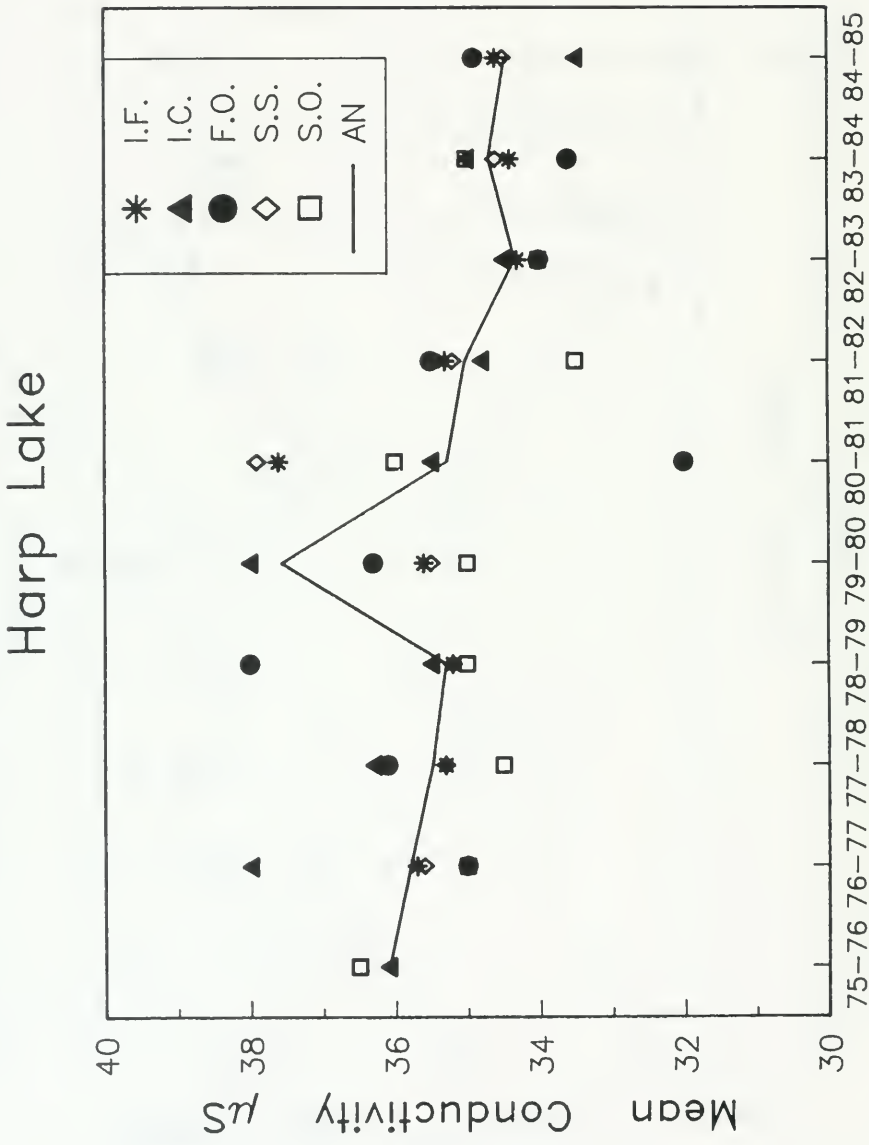

Harp Lake
Mean Conductivity μS
40
38
36
34
32
30
I.F.
I.C.
F.O.
S.S.
S.O.
AN
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 3.b

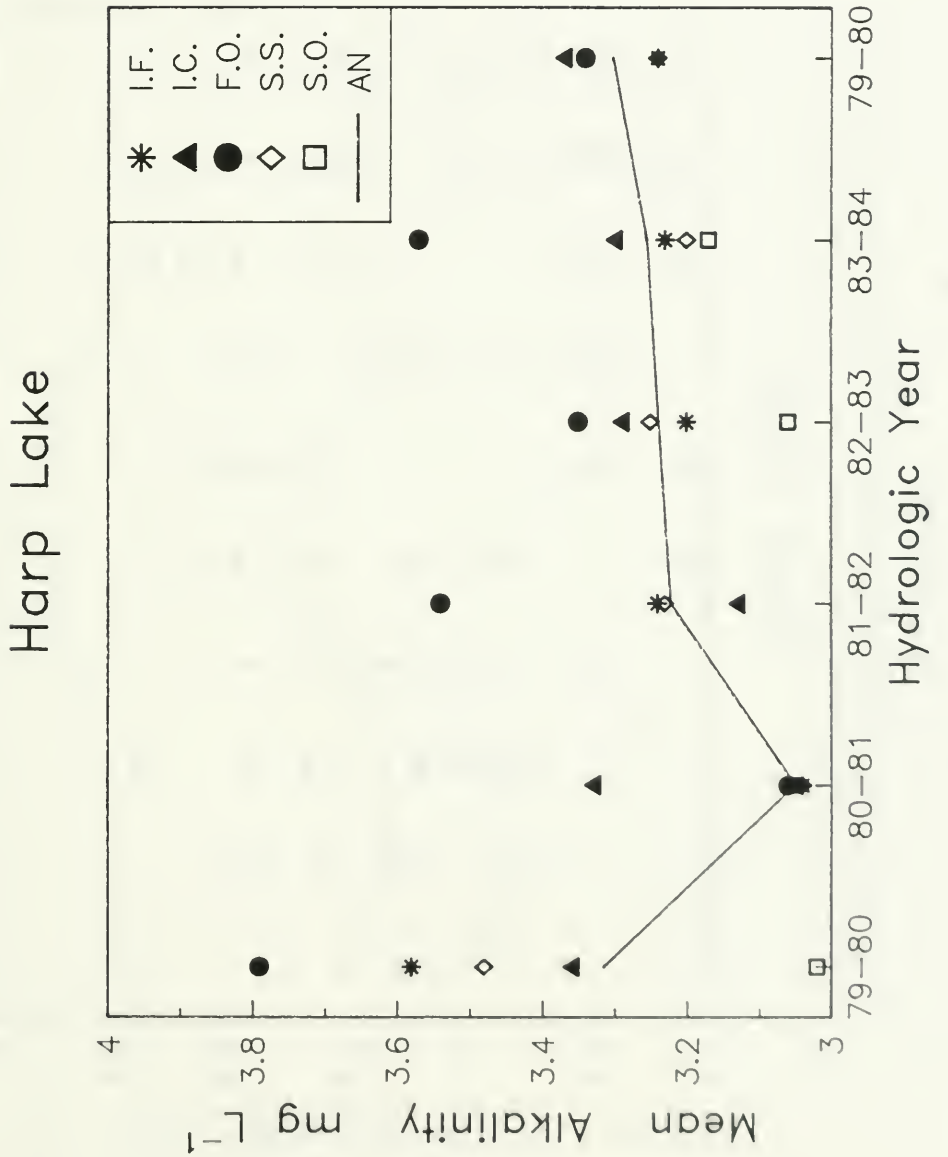

Harp Lake
Mean Alkalinity mg L⁻¹
4
3.8
3.6
3.4
3.2
3
79–80
80–81
81–82
82–83
83–84
79–80
Hydrologic Year
I.F.
I.C.
F.O.
S.S.
S.O.
AN

Fig. 3.c

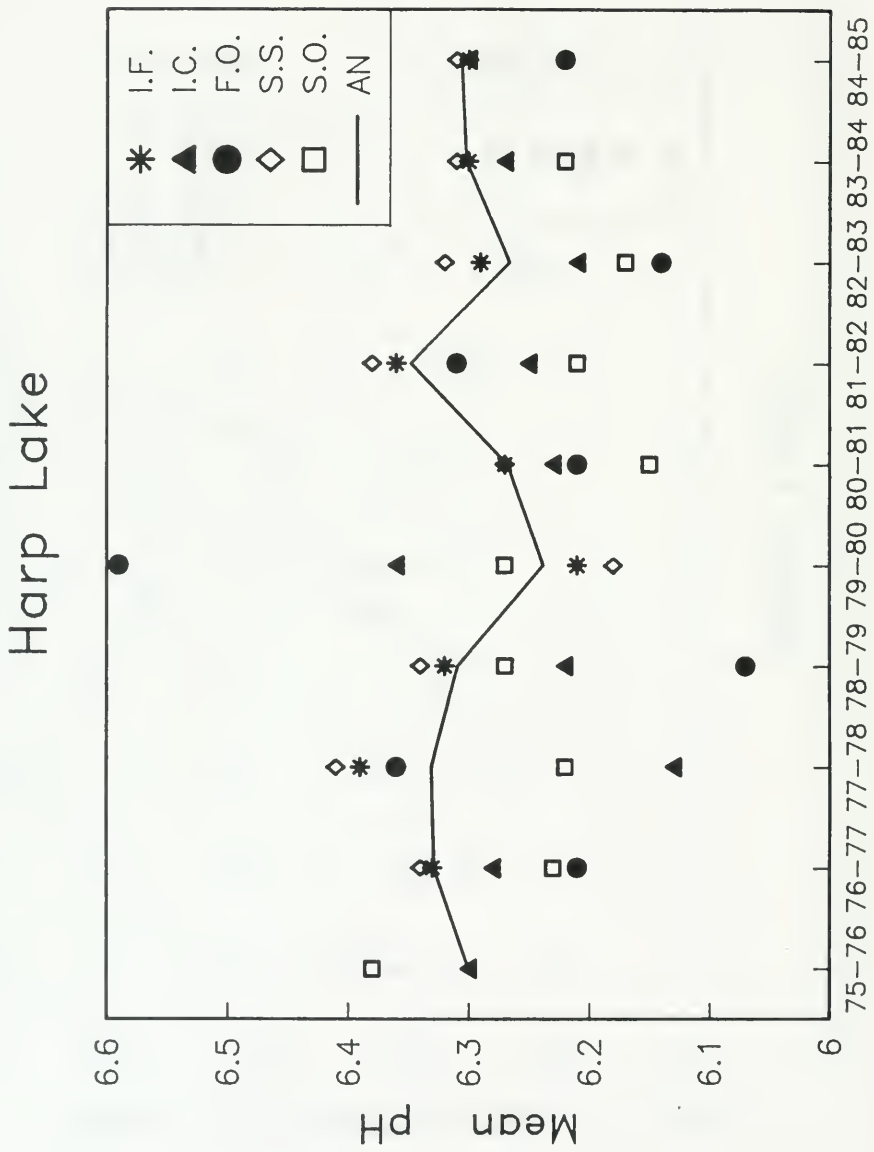

Harp Lake
Mean pH
6.6
6.5
6.4
6.3
6.2
6.1
6
I.F.
I.C.
F.O.
S.S.
S.O.
AN
75-76 76-77 77-78 78-79 79-80 80-81 81-82 82-83 83-84 84-85
Hydrologic Year

Fig. 3.d

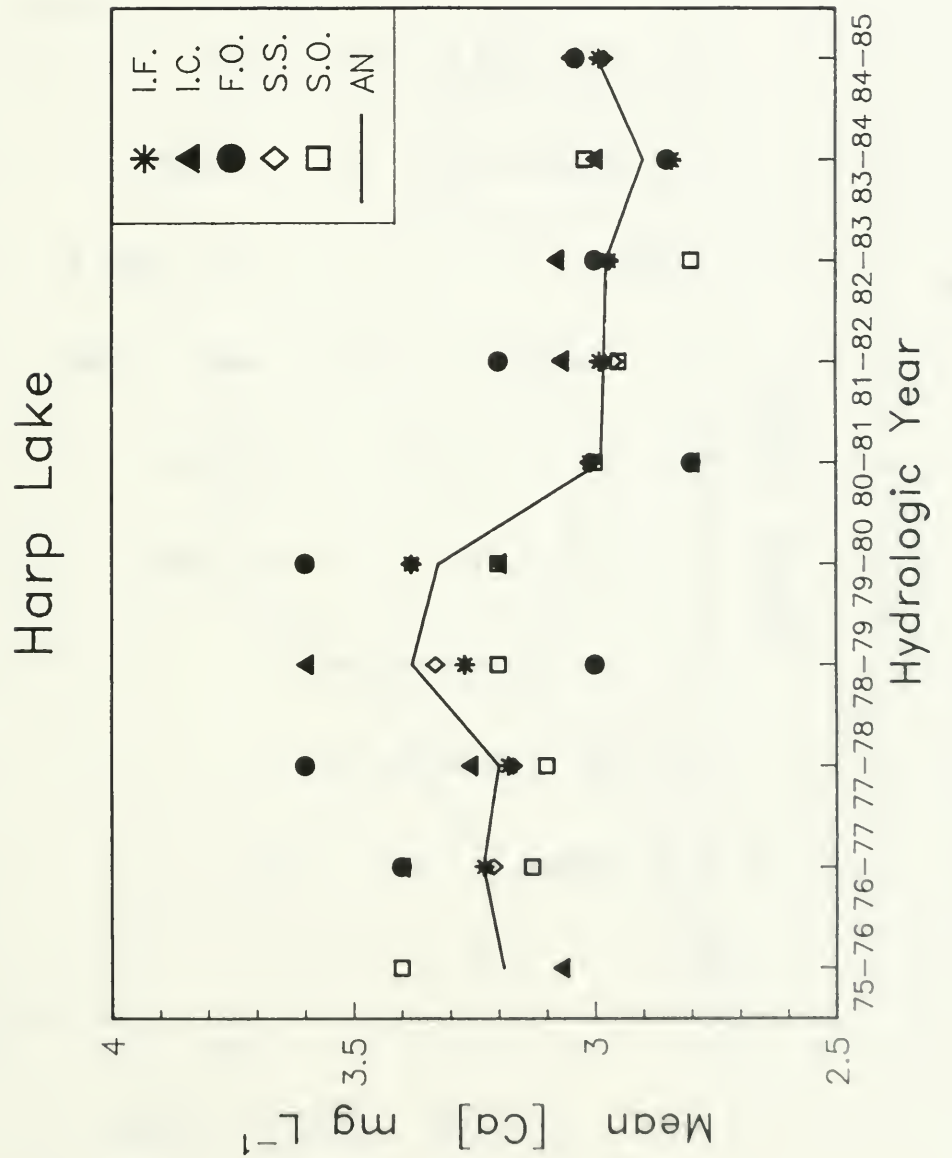

Harp Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
4
3.5
3
2.5
Mean [Ca] mg L⁻¹
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 3.e

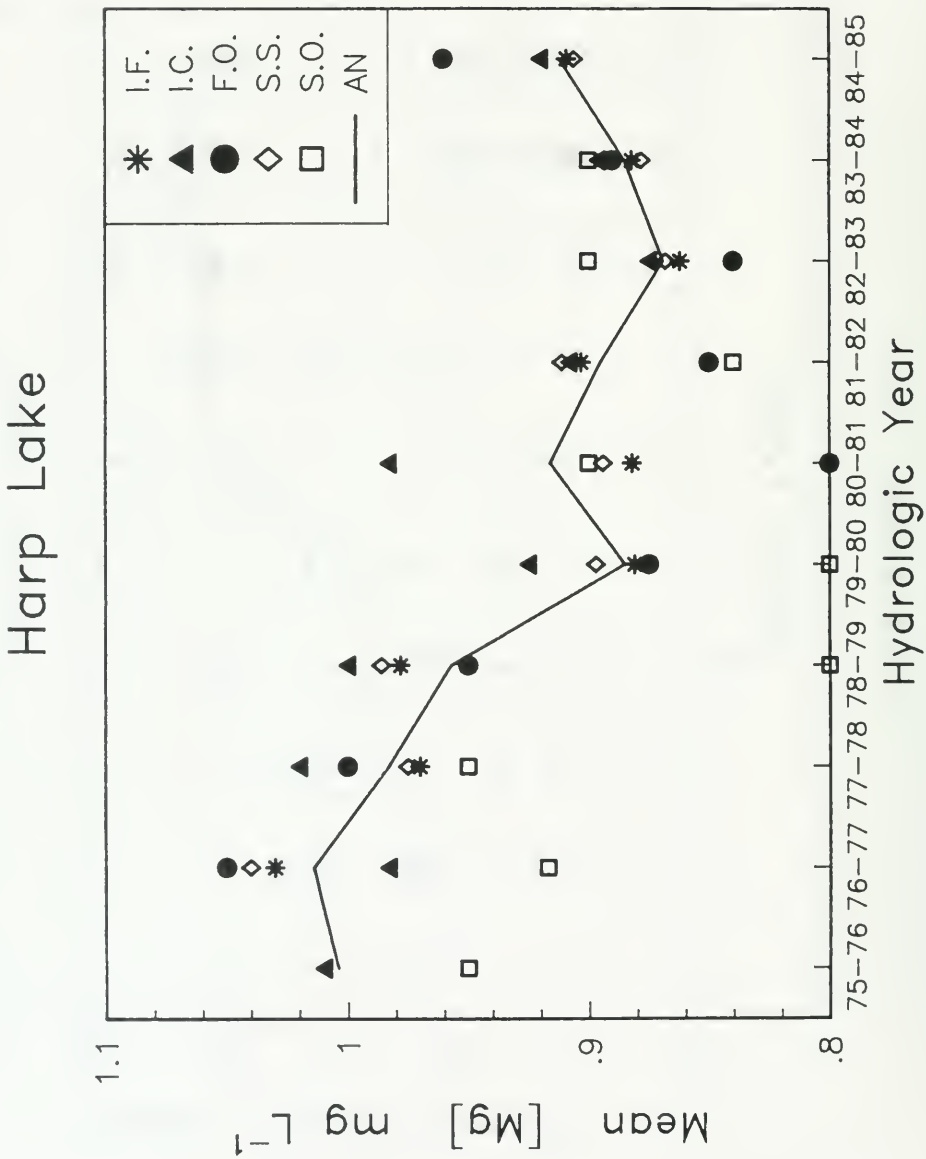

Harp Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [Mg] mg L⁻¹
1.1
1
.9
.8
75-76 76-77 77-78 78-79 79-80 80-81 81-82 82-83 83-84 84-85
Hydrologic Year

Fig. 3.f

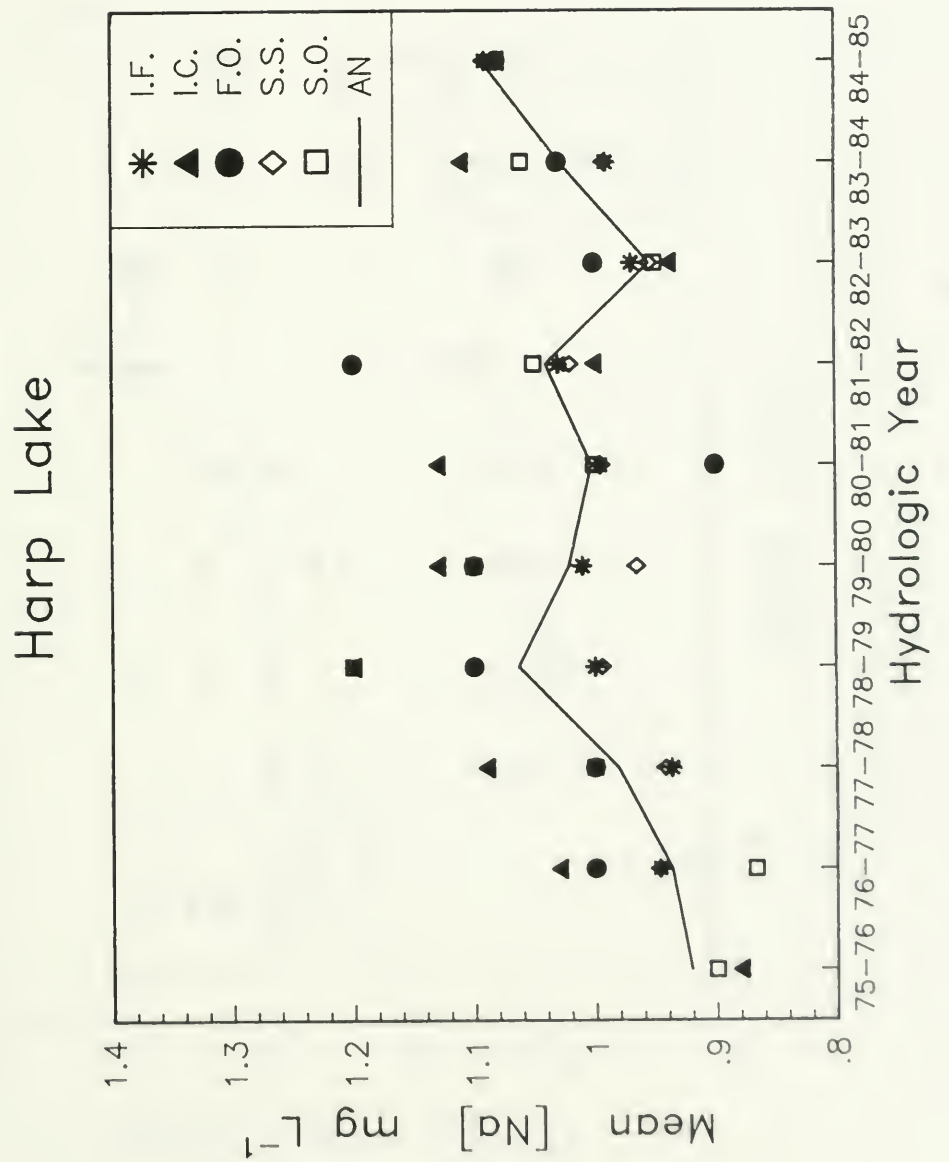

Harp Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [Na] mg L⁻¹
1.4
1.3
1.2
1.1
1
.9
.8
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 3.g

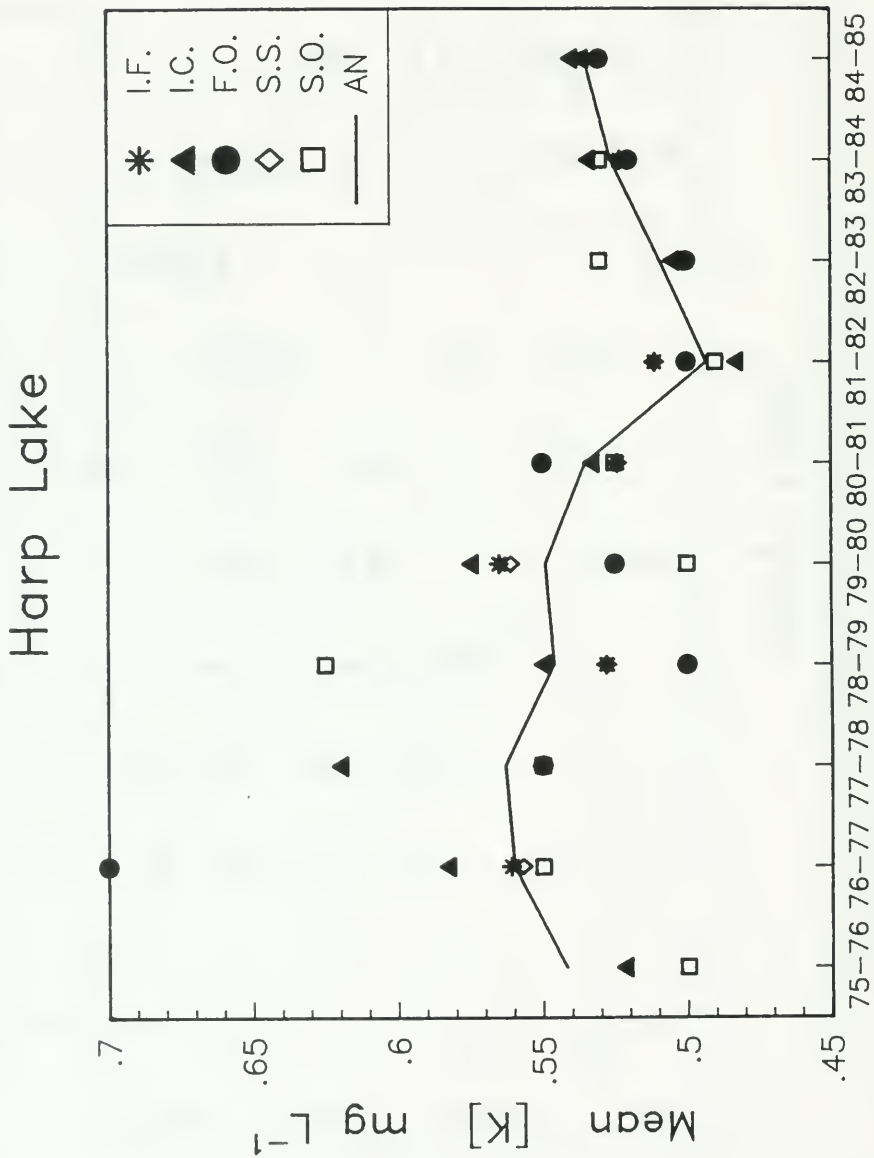

Harp Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [K] mg L⁻¹
.7
.65
.6
.55
.5
.45
75-76 76-77 77-78 78-79 79-80 80-81 81-82 82-83 83-84 84-85
Hydrologic Year

Fig. 3.h

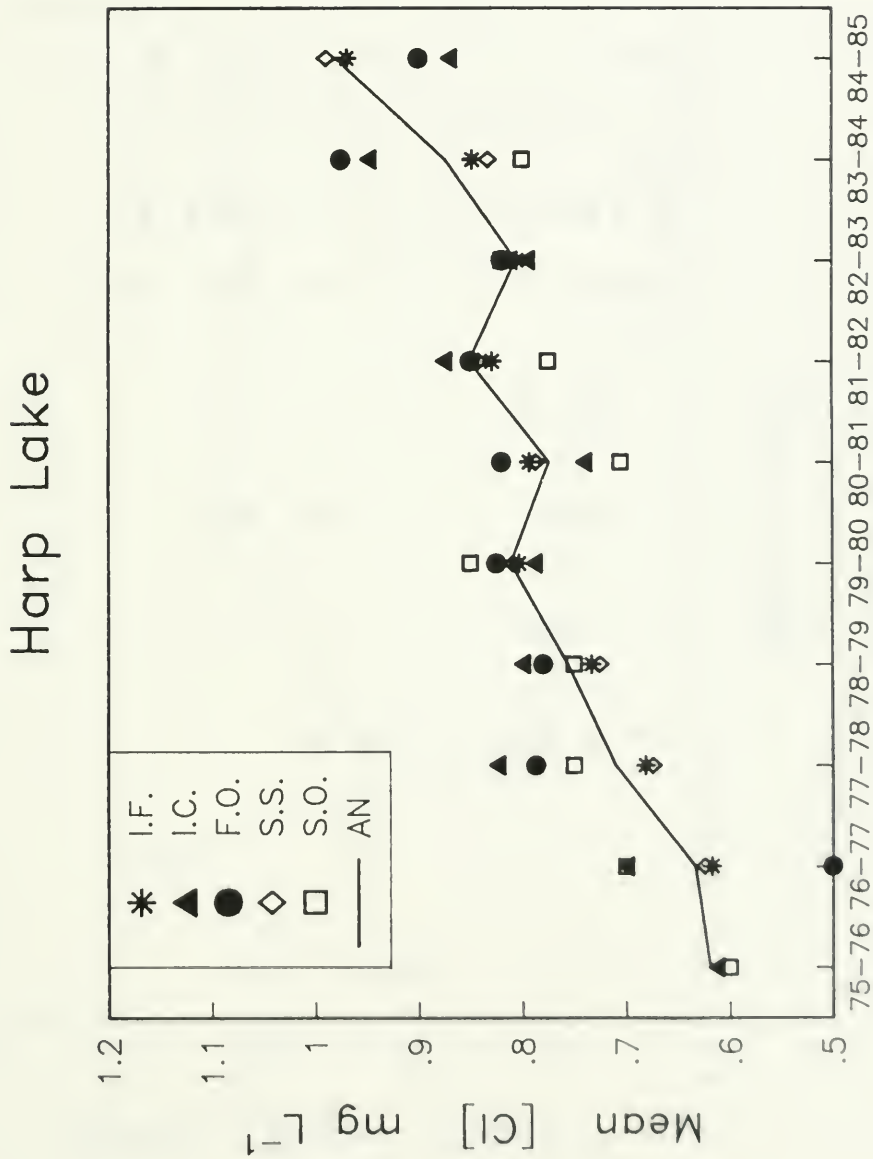

Harp Lake
Mean [Cl] mg L⁻¹
1.2
1.1
1
.9
.8
.7
.6
.5
I.F.
I.C.
F.O.
S.S.
S.O.
AN
75–76 76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 3.i

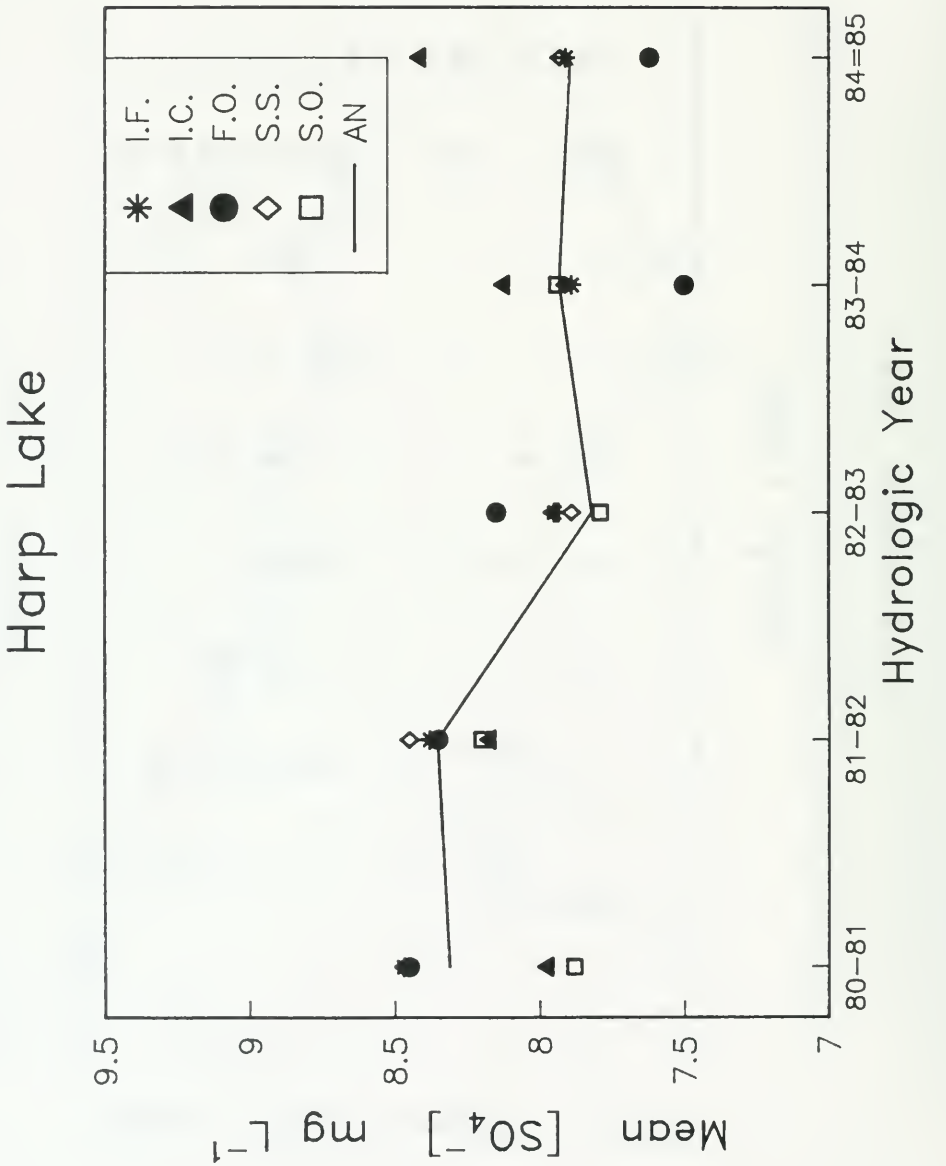

Harp Lake
Mean [SO4-] mg L-1
9.5
9
8.5
8
7.5
7
80-81
81-82
82-83
83-84
84-85
Hydrologic Year
I.F.
I.C.
F.O.
S.S.
S.O.
AN

Fig. 3.j

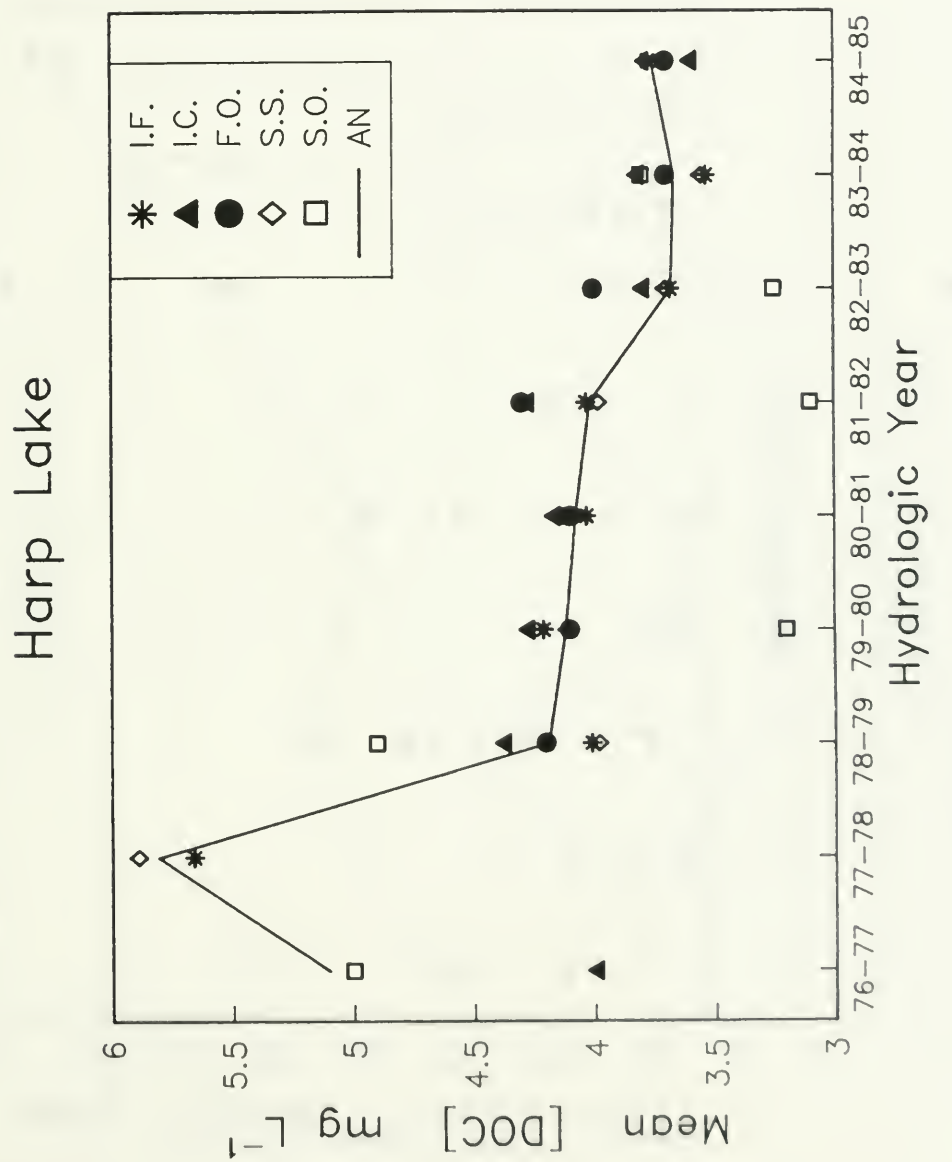

Harp Lake
I.F.
I.C.
F.O.
S.S.
S.O.
AN
Mean [DOC] mg L⁻¹
6
5.5
5
4.5
4
3.5
3
76–77 77–78 78–79 79–80 80–81 81–82 82–83 83–84 84–85
Hydrologic Year

Fig. 3.k

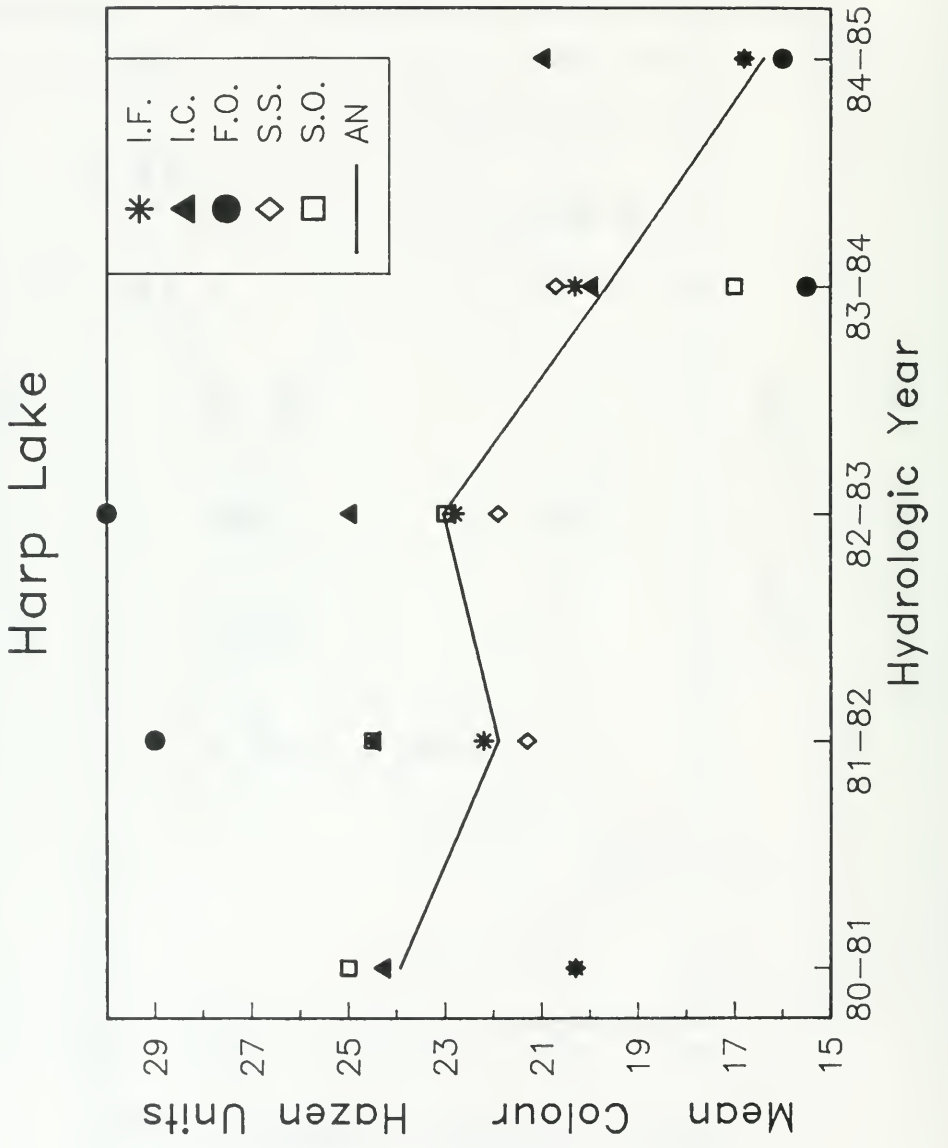

Harp Lake
Mean Colour Hazen Units
29
27
25
23
21
19
17
15
80–81
81–82
82–83
83–84
84–85
Hydrologic Year
I.F.
I.C.
F.O.
S.S.
S.O.
AN

Fig. 3.1

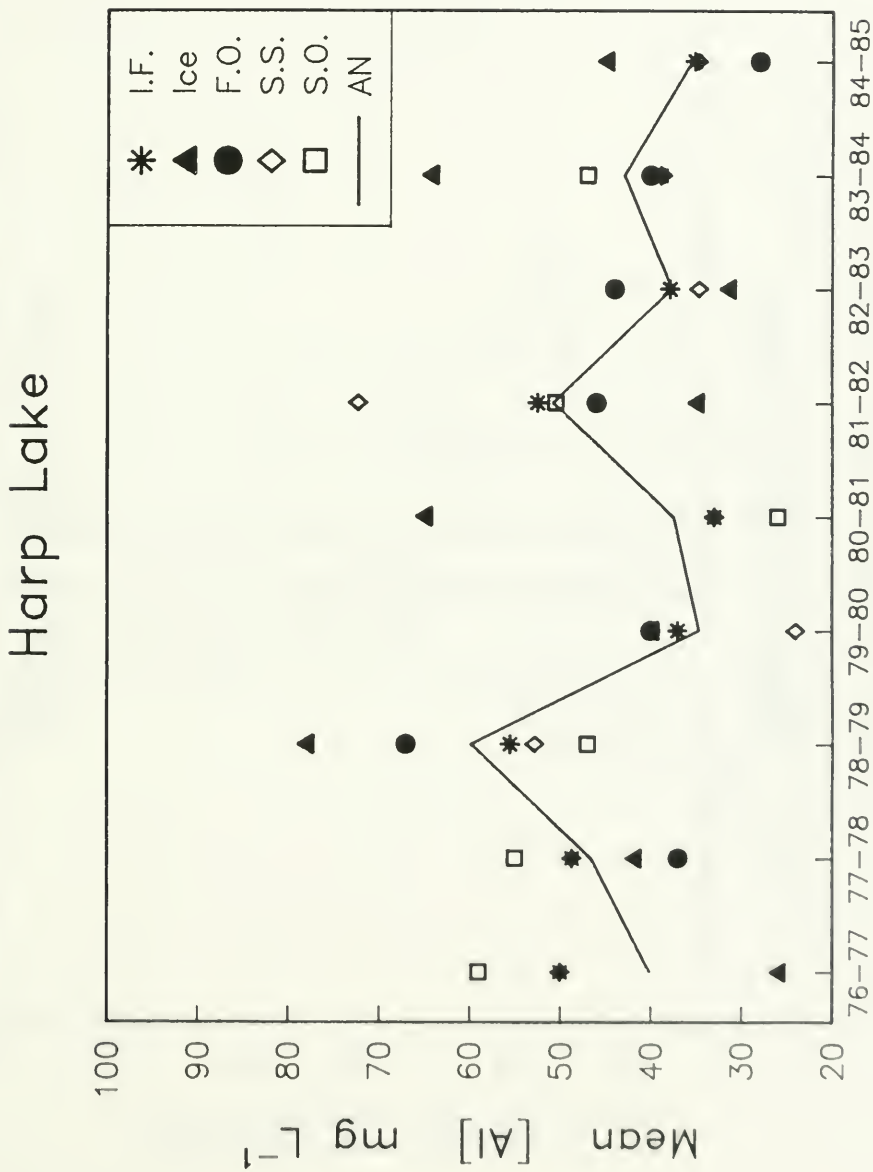
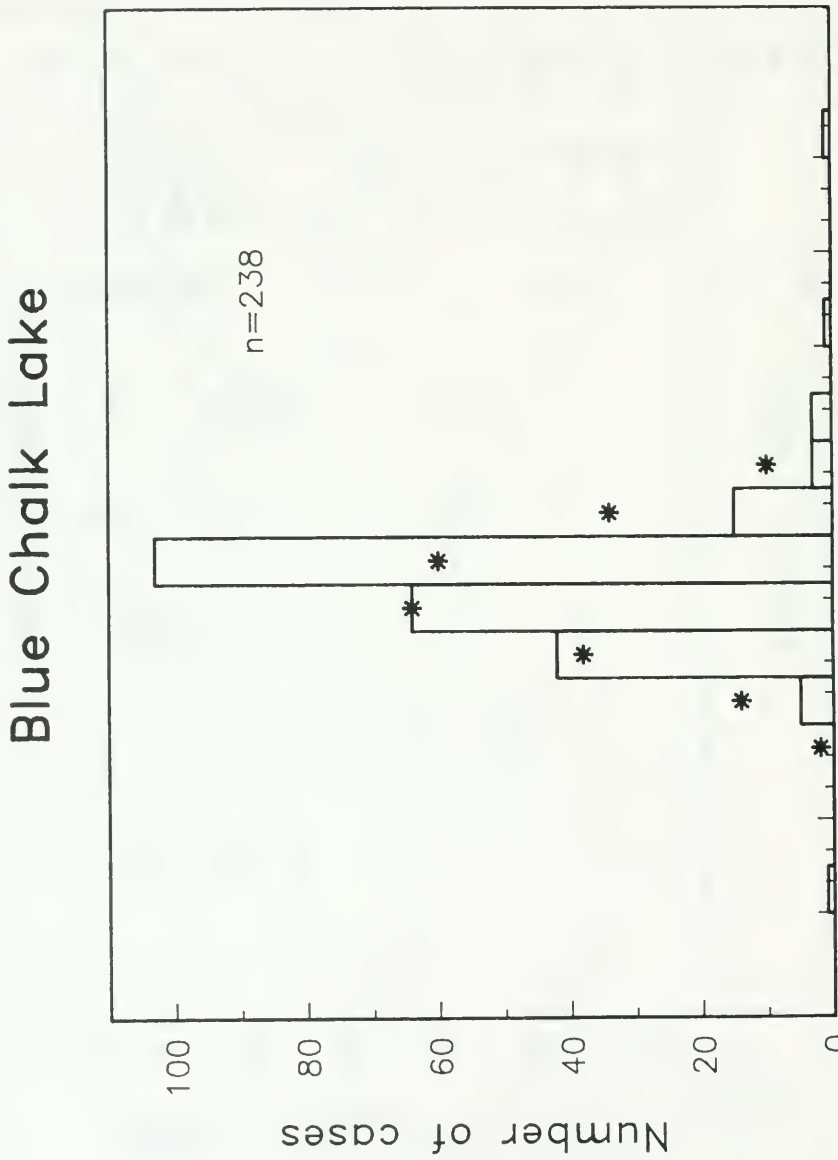

Harp Lake
I.F.
Ice
F.O.
S.S.
S.O.
AN
Mean [Al] mg L⁻¹
100
90
80
70
60
50
40
30
20
76–77
77–78
78–79
79–80
80–81
81–82
82–83
83–84
84–85
Hydrologic Year

Fig. 4.a


Blue Chalk Lake
n=238
Number of cases
0
20
40
60
80
100
23
25
27
29
31
33
35
37
39
Conductivity µS

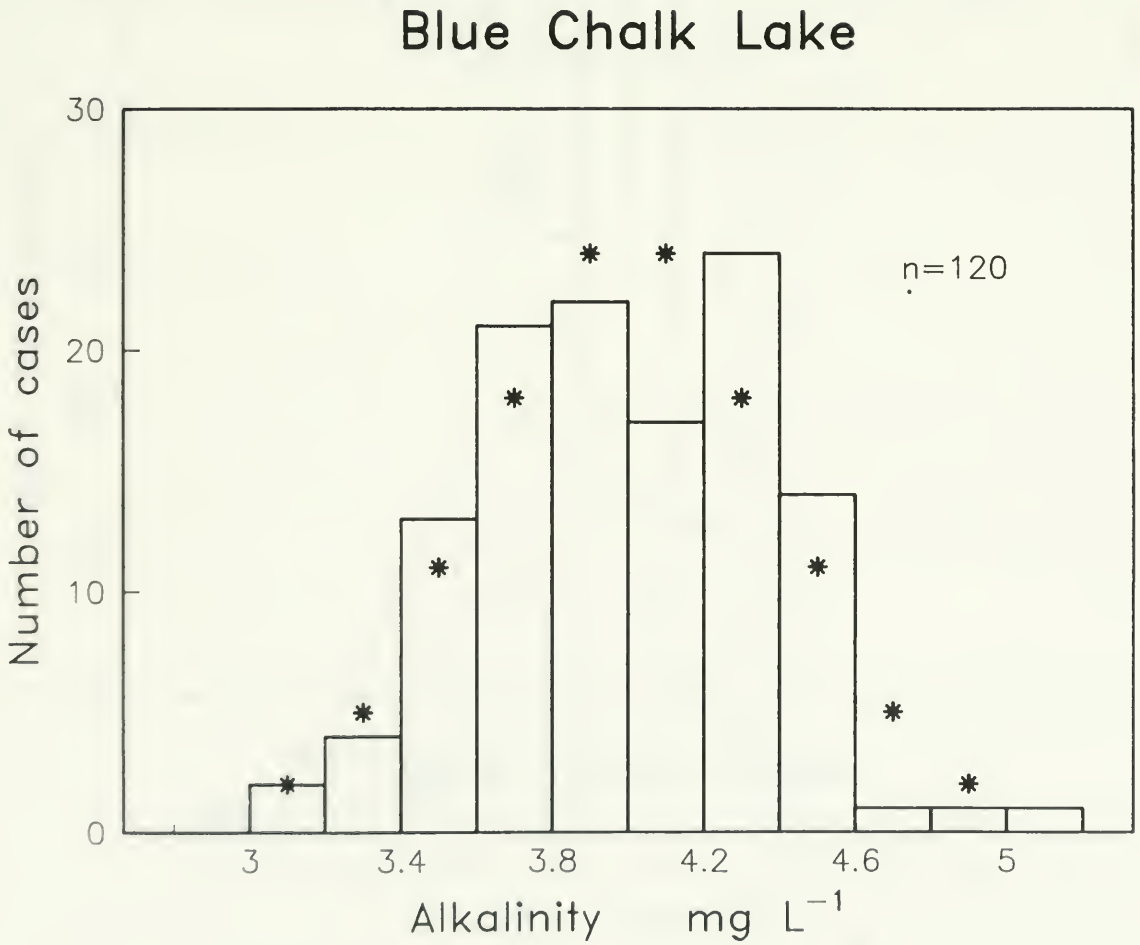

Blue Chalk Lake
30
20
10
0
Number of cases
n=120
3
3.4
3.8
4.2
4.6
5
Alkalinity mg L^{-1}

Fig. 4.b

Fig. 4.c

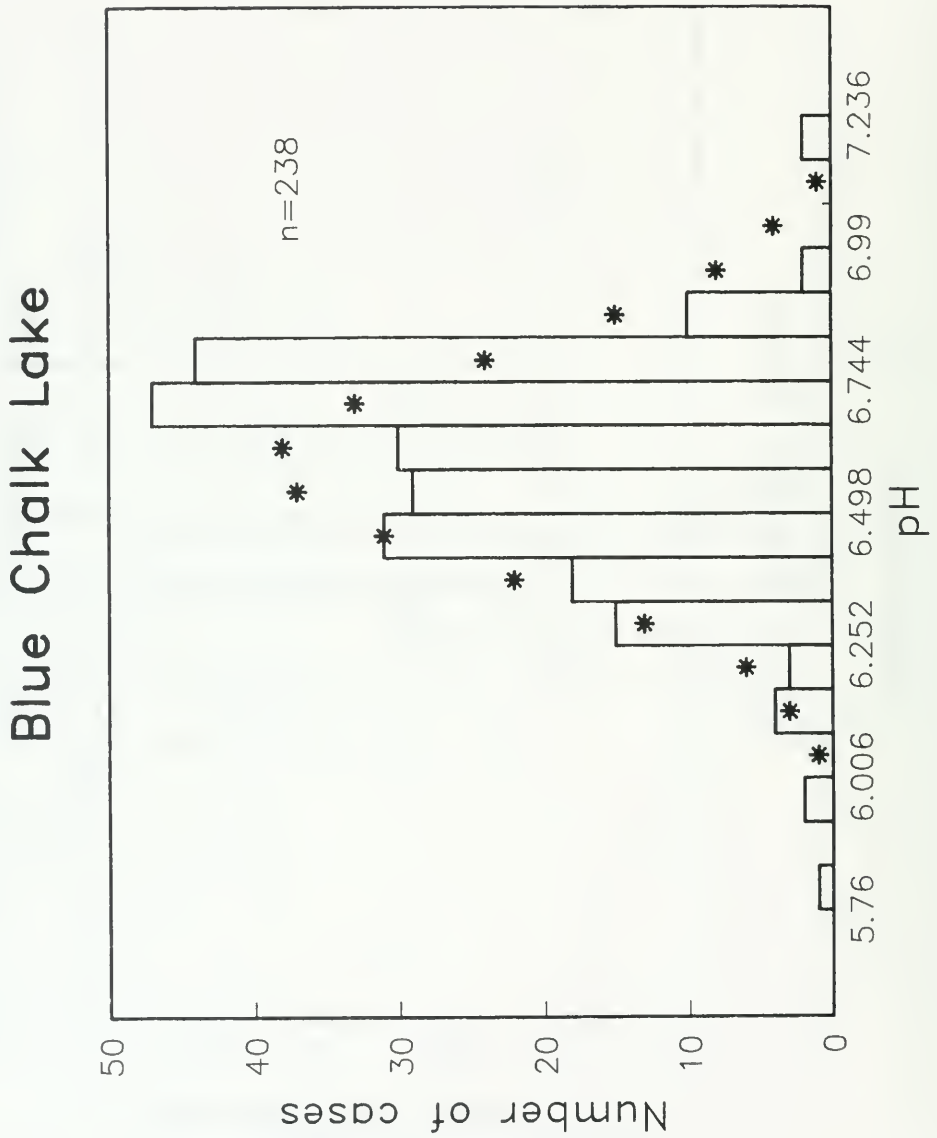

Blue Chalk Lake
n=238
Number of cases
0
10
20
30
40
50
5.76
6.006
6.252
6.498
6.744
6.99
7.236
pH

Fig. 4.d

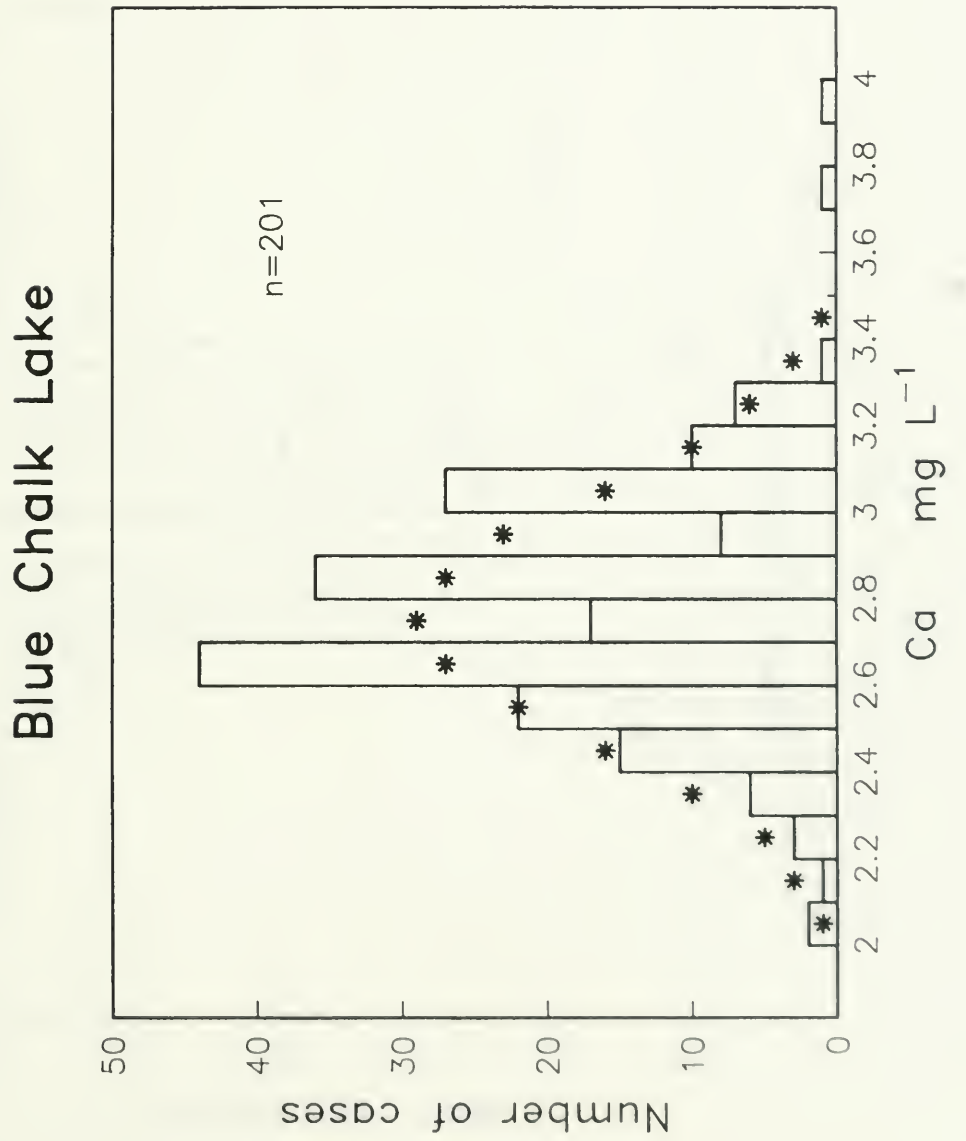

Blue Chalk Lake
n=201
Number of cases
0
10
20
30
40
50
2
2.2
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
4
Ca mg L^{-1}

Fig. 4.e

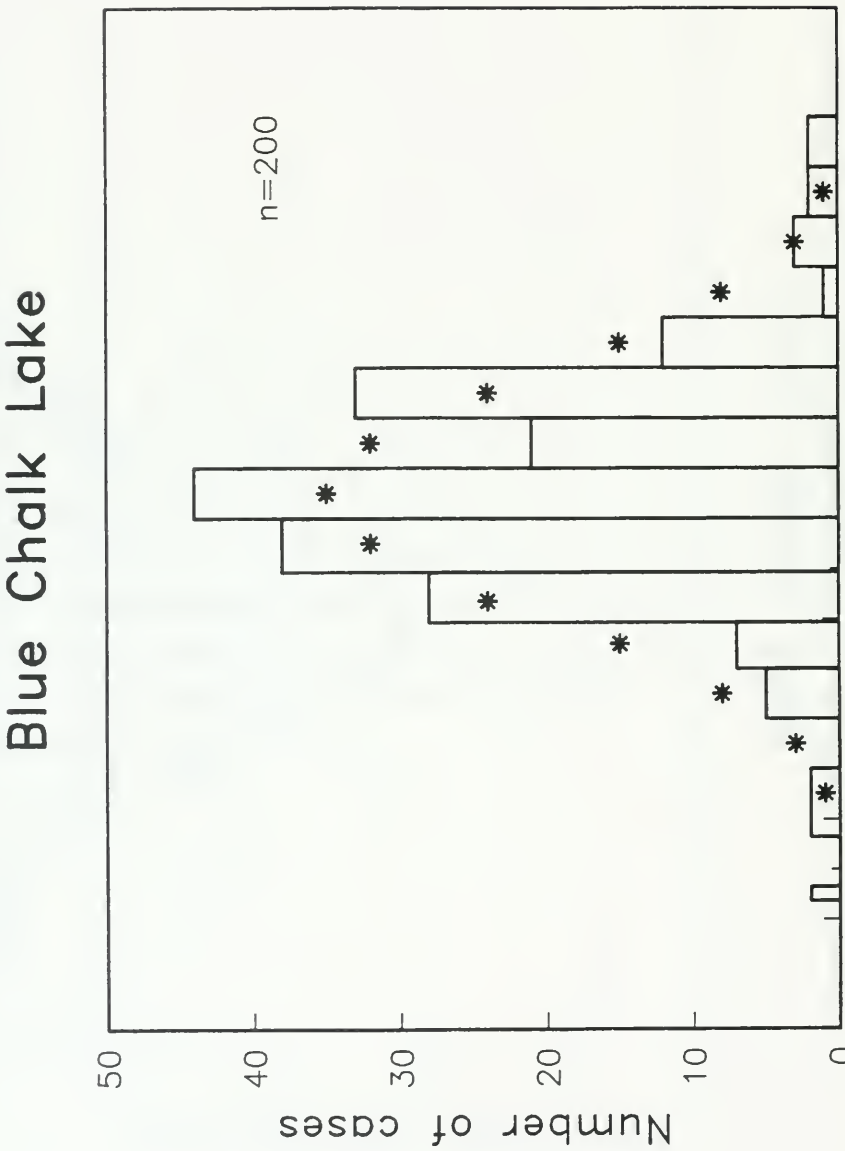

Blue Chalk Lake
n=200
Number of cases
0
10
20
30
40
50
.44
.51
.58
.65
.72
.79
.86
.93
1
Mg mg L^{-1}

Fig. 4.f

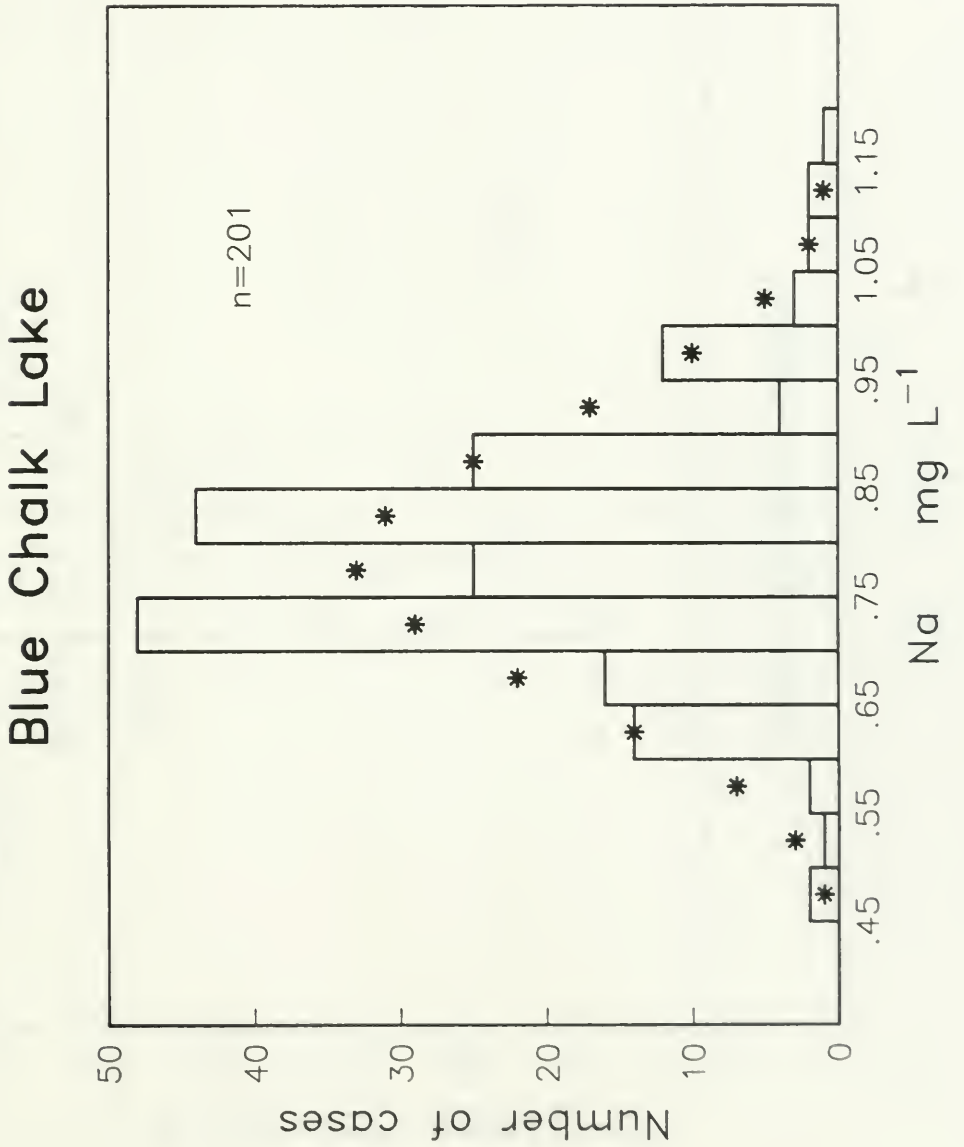

Blue Chalk Lake
n=201
Number of cases
0
10
20
30
40
50
.45
.55
.65
.75
.85
.95
1.05
1.15
Na mg L^{-1}

Fig. 4.g

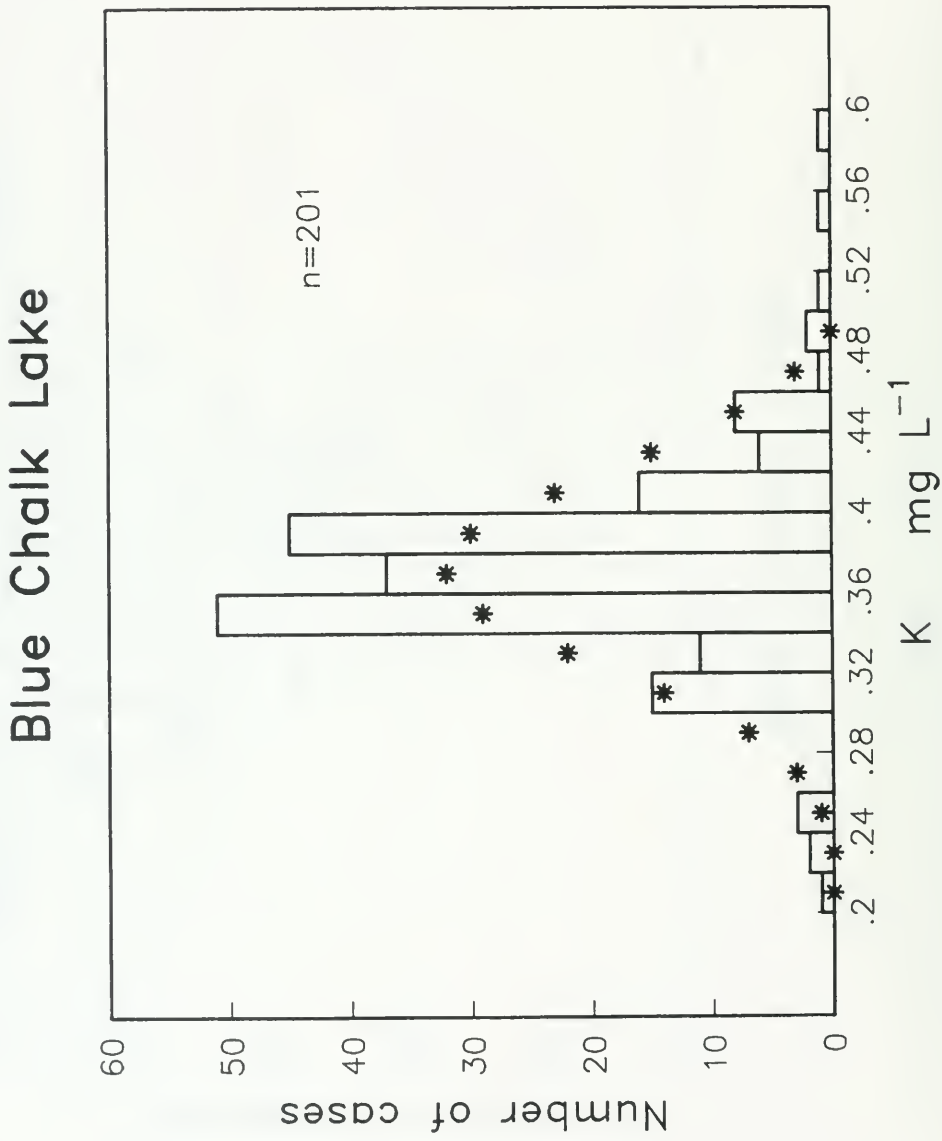

Blue Chalk Lake
n=201
Number of cases
0
10
20
30
40
50
60
.2
.24
.28
.32
.36
.4
.44
.48
.52
.56
.6
K mg L^{-1}

Fig. 4.h

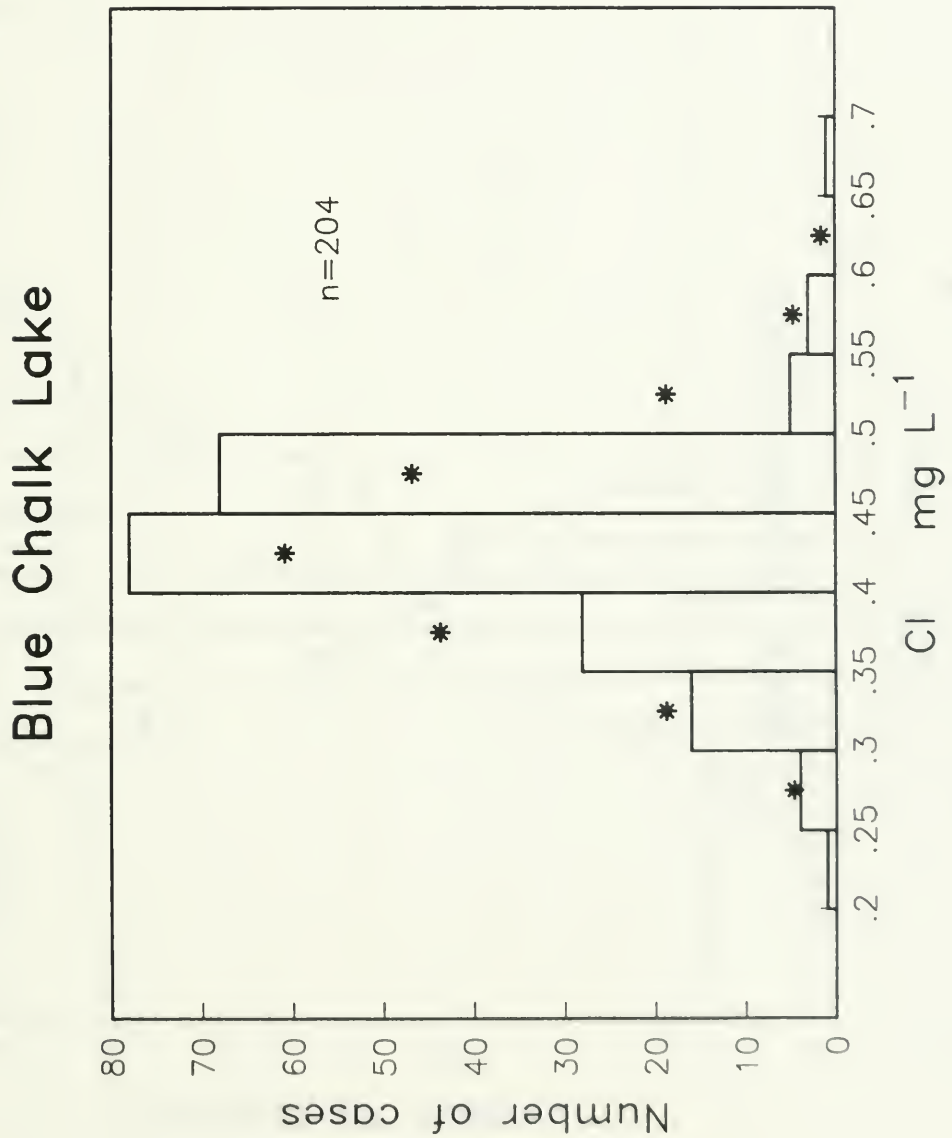

Blue Chalk Lake
n=204
Number of cases
0
10
20
30
40
50
60
70
80
.2
.25
.3
.35
.4
.45
.5
.55
.6
.65
.7
Cl mg L^{-1}

Fig. 4.i

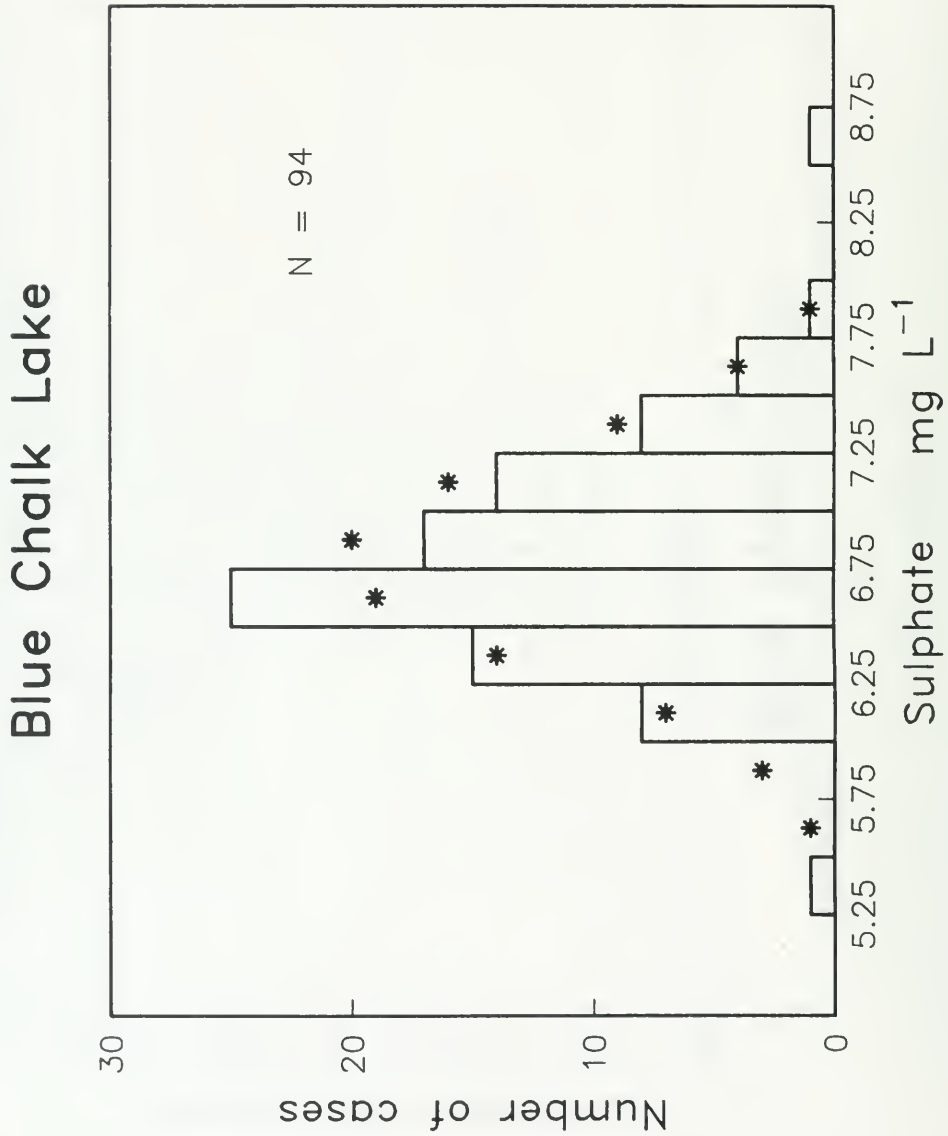

Blue Chalk Lake
N = 94
Number of cases
0
10
20
30
5.25
5.75
6.25
6.75
7.25
7.75
8.25
8.75
Sulphate mg L⁻¹

Fig. 4.j

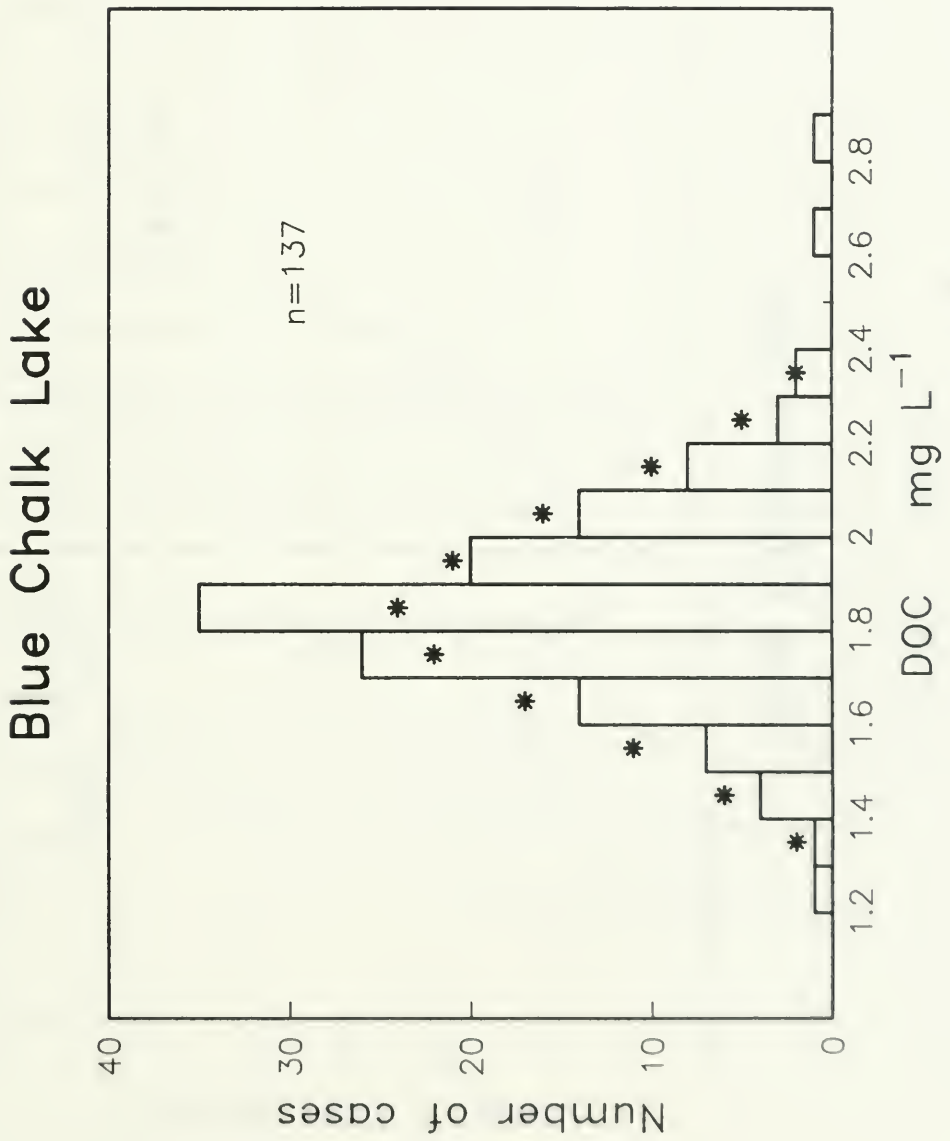

Blue Chalk Lake
n=137
Number of cases
0
10
20
30
40
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
DOC mg L^{-1}

Fig. 4.k

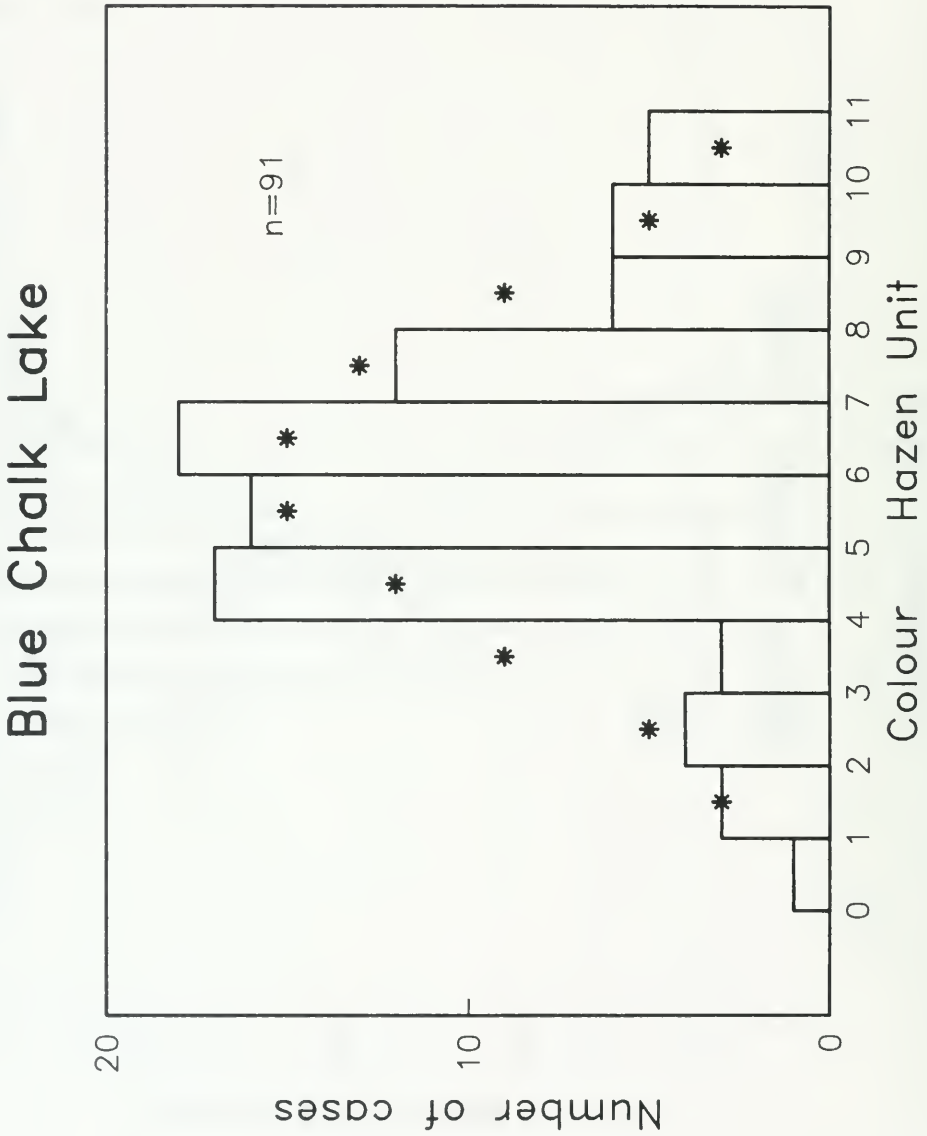

Blue Chalk Lake
n=91
Number of cases
0
10
20
0 1 2 3 4 5 6 7 8 9 10 11
Colour Hazen Unit

Fig. 4.1

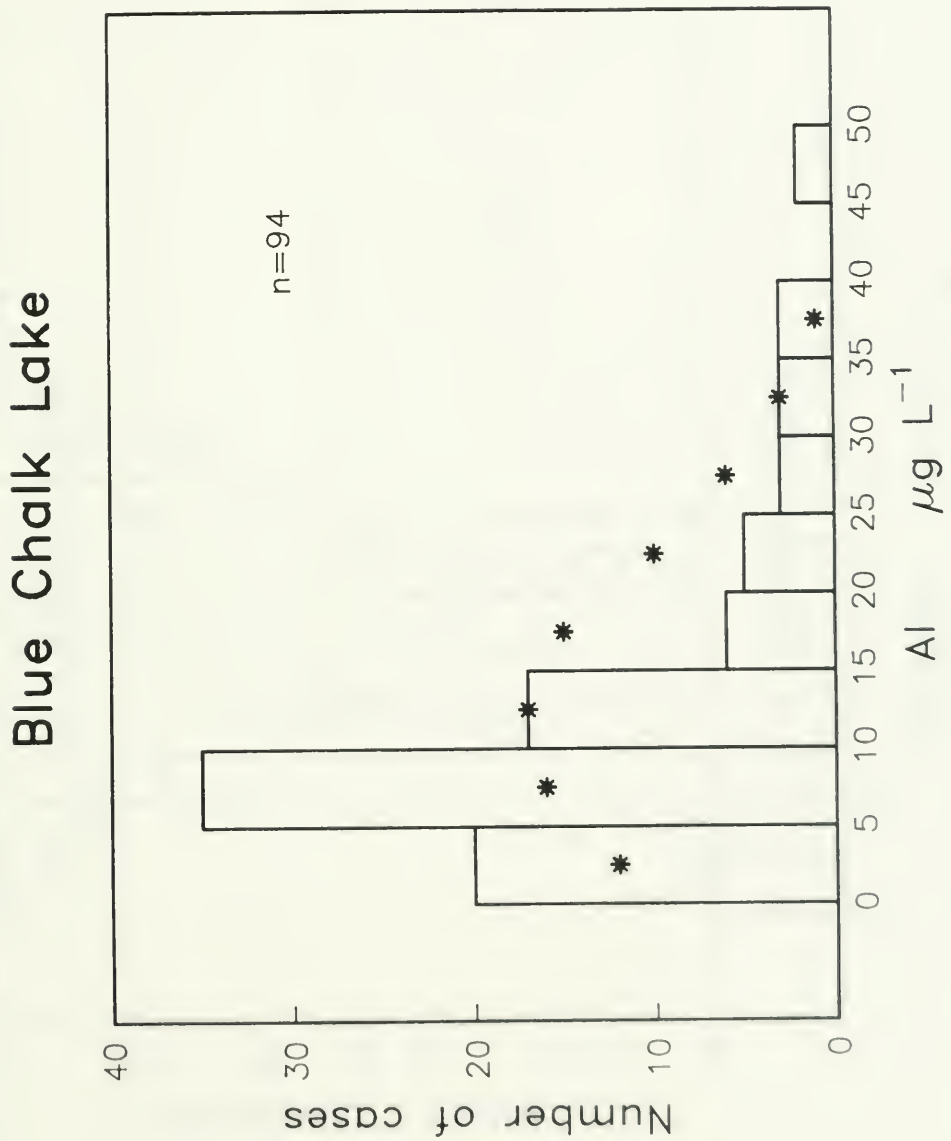

Blue Chalk Lake
n=94
Number of cases
0
10
20
30
40
0 5 10 15 20 25 30 35 40 45 50
Al μg L⁻¹

Fig. 5.a

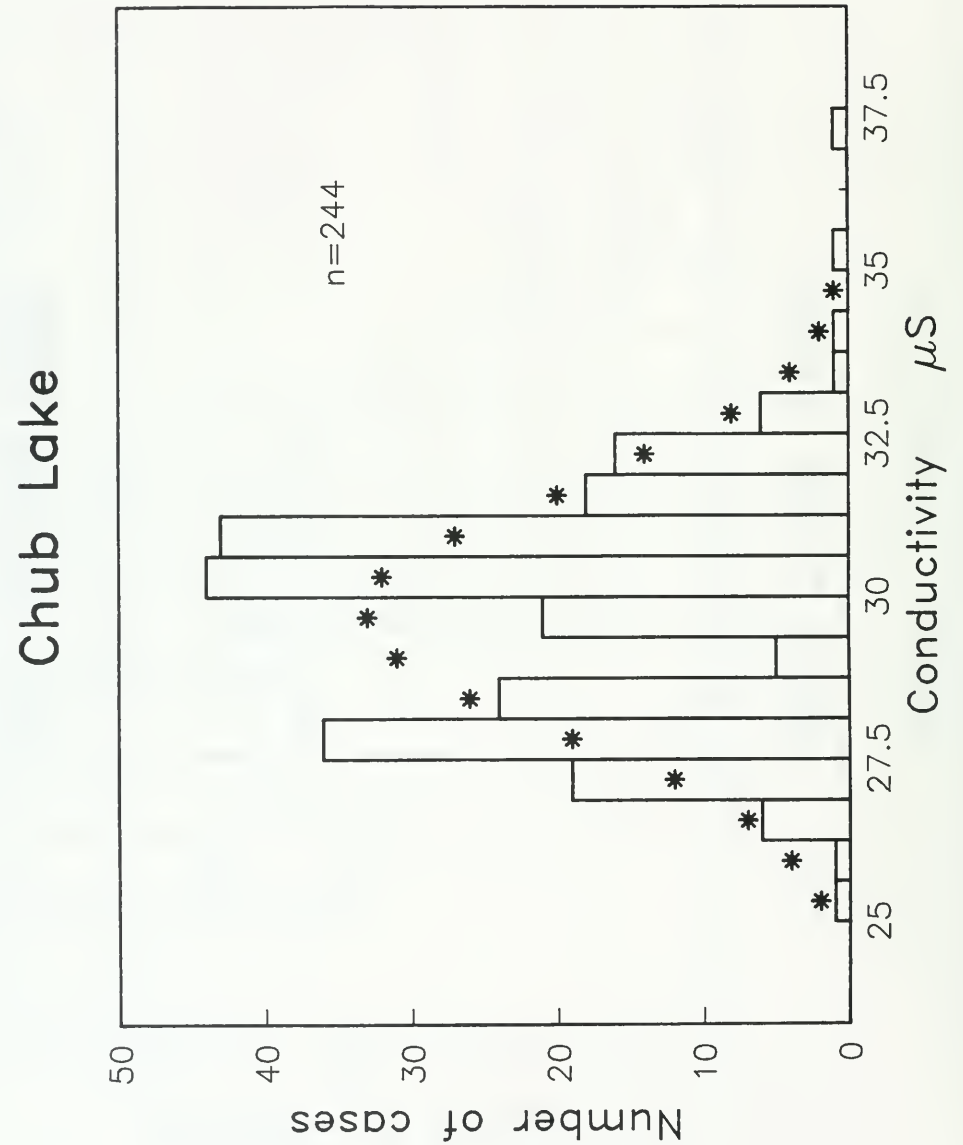

Chub Lake
n=244
Number of cases
0
10
20
30
40
50
25
27.5
30
32.5
35
37.5
Conductivity μS

Fig. 5.b

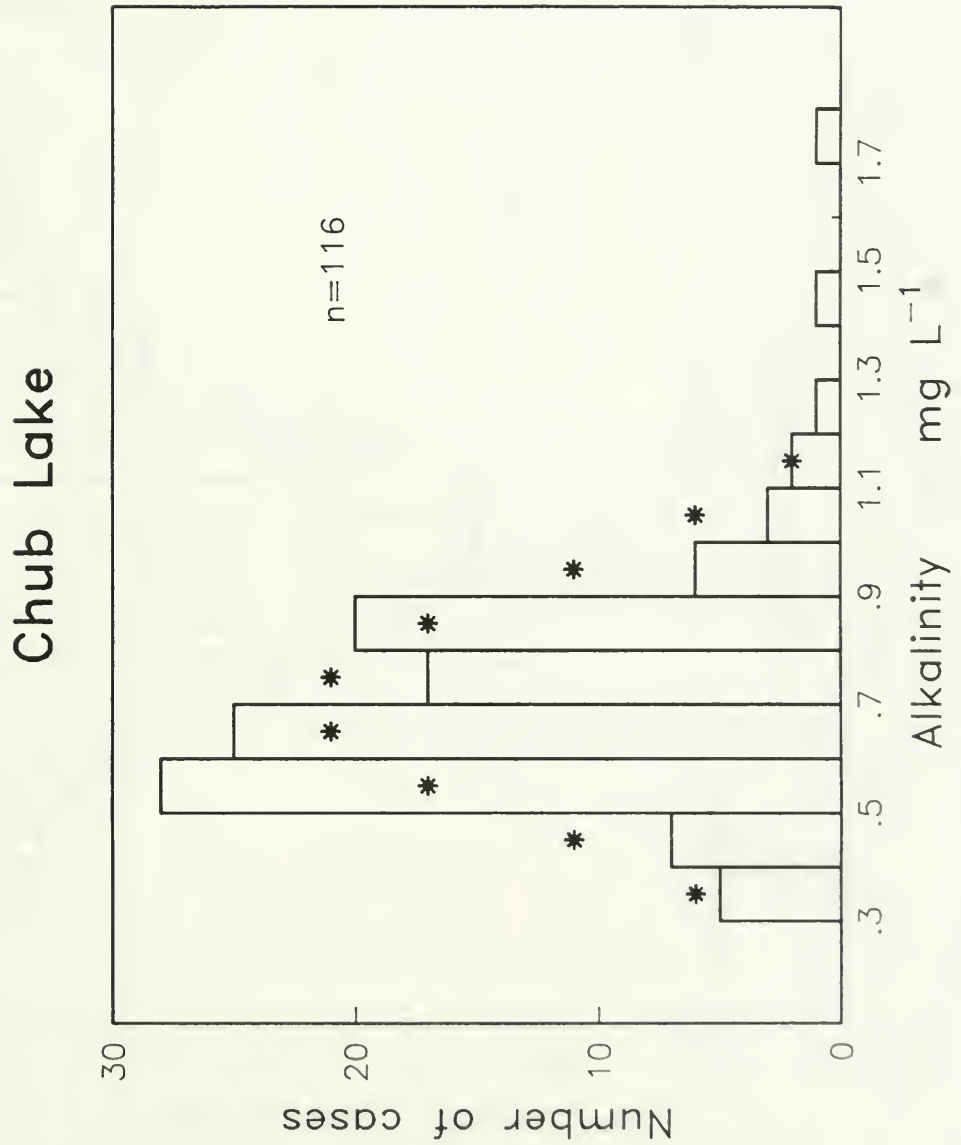

Chub Lake
n=116
Number of cases
0
10
20
30
.3
.5
.7
.9
1.1
1.3
1.5
1.7
Alkalinity mg L^{-1}

Fig. 5.c

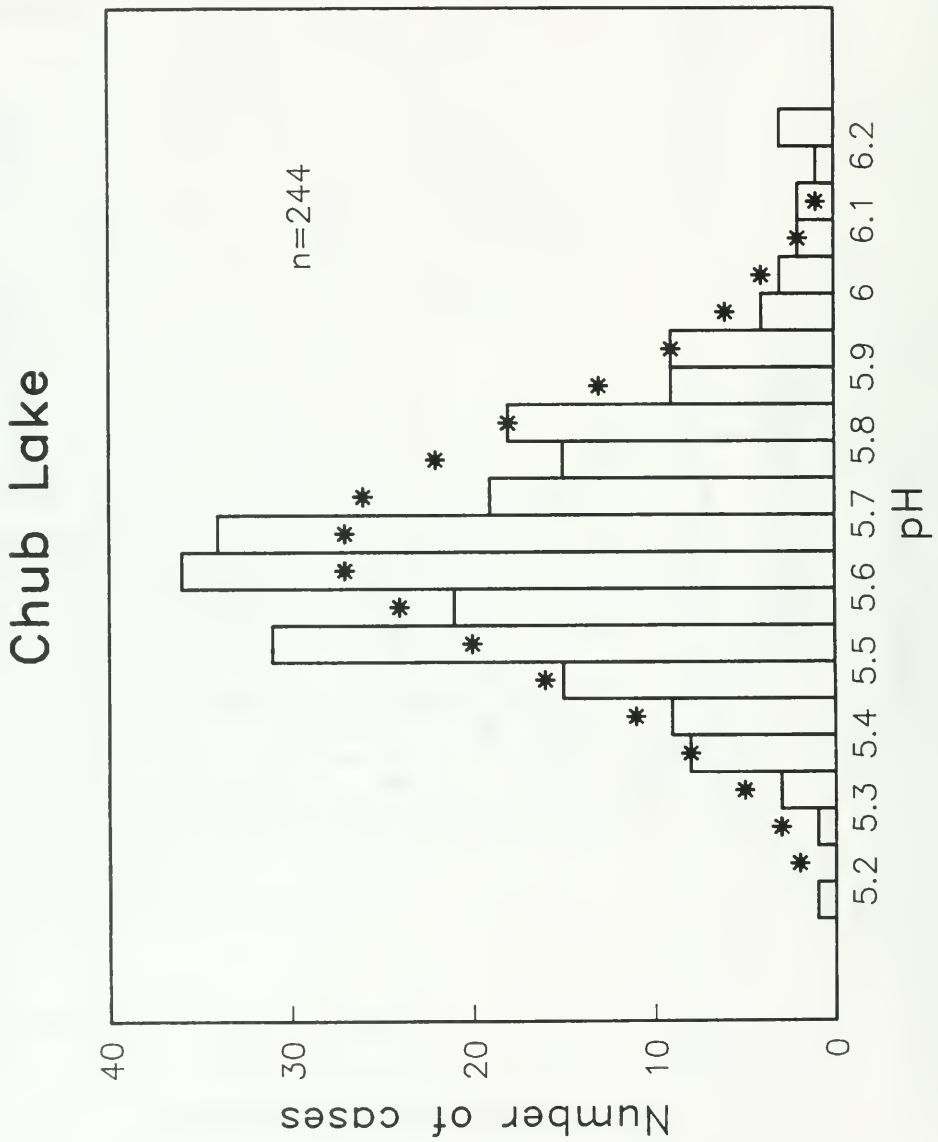

Chub Lake
n=244
Number of cases
0
10
20
30
40
5.2
5.3
5.4
5.5
5.6
5.7
5.8
5.9
6
6.1
6.2
pH

Fig. 5.d

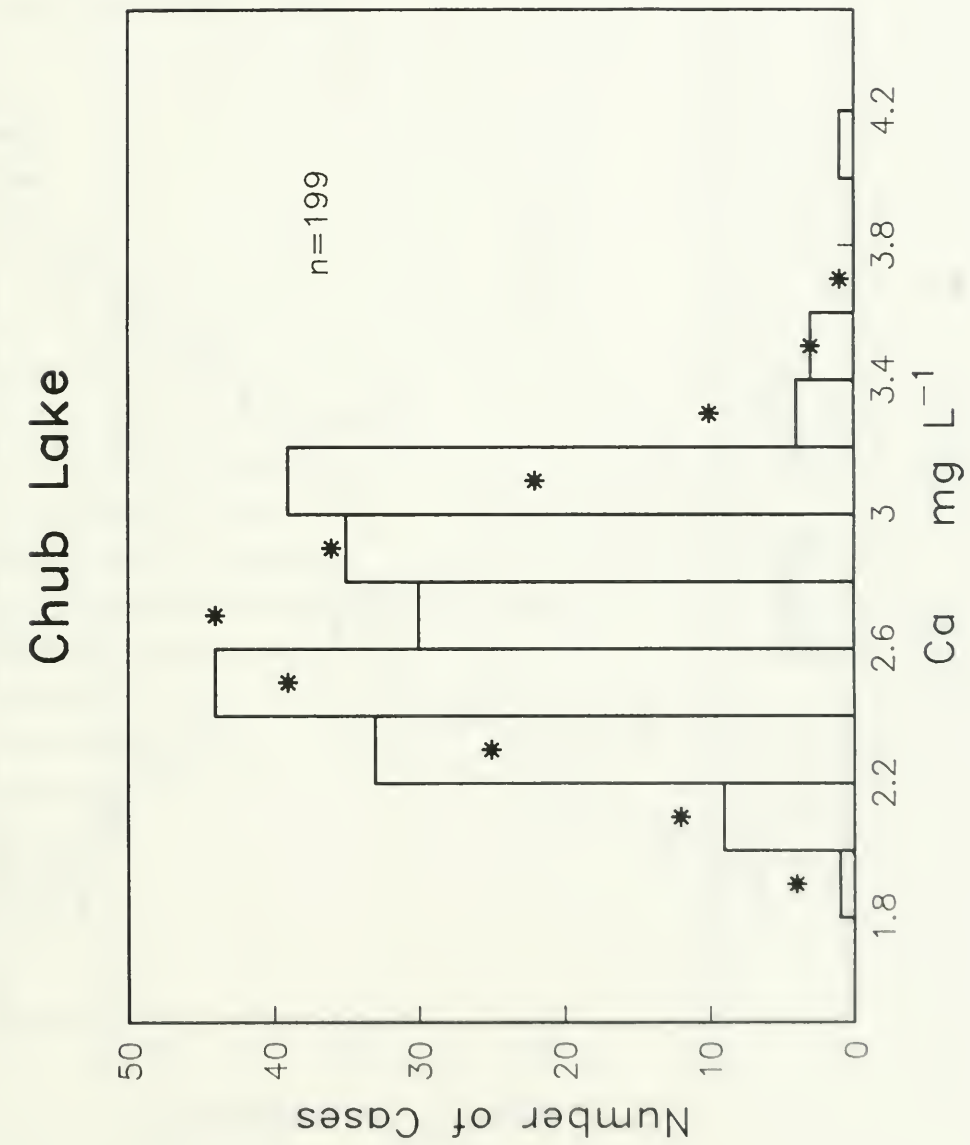

Chub Lake
n=199
Number of Cases
0
10
20
30
40
50
1.8
2.2
2.6
3
3.4
3.8
4.2
Ca mg L^{-1}

Fig. 5.e

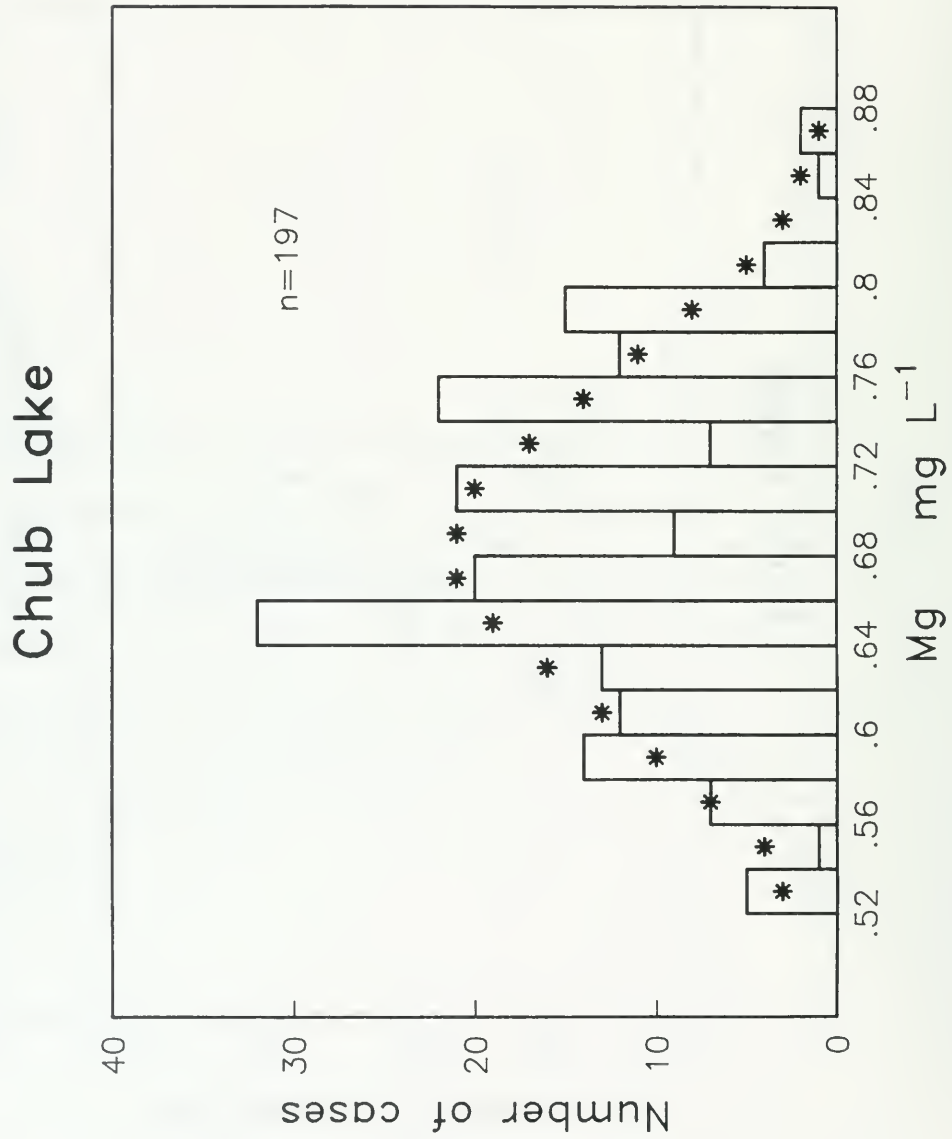
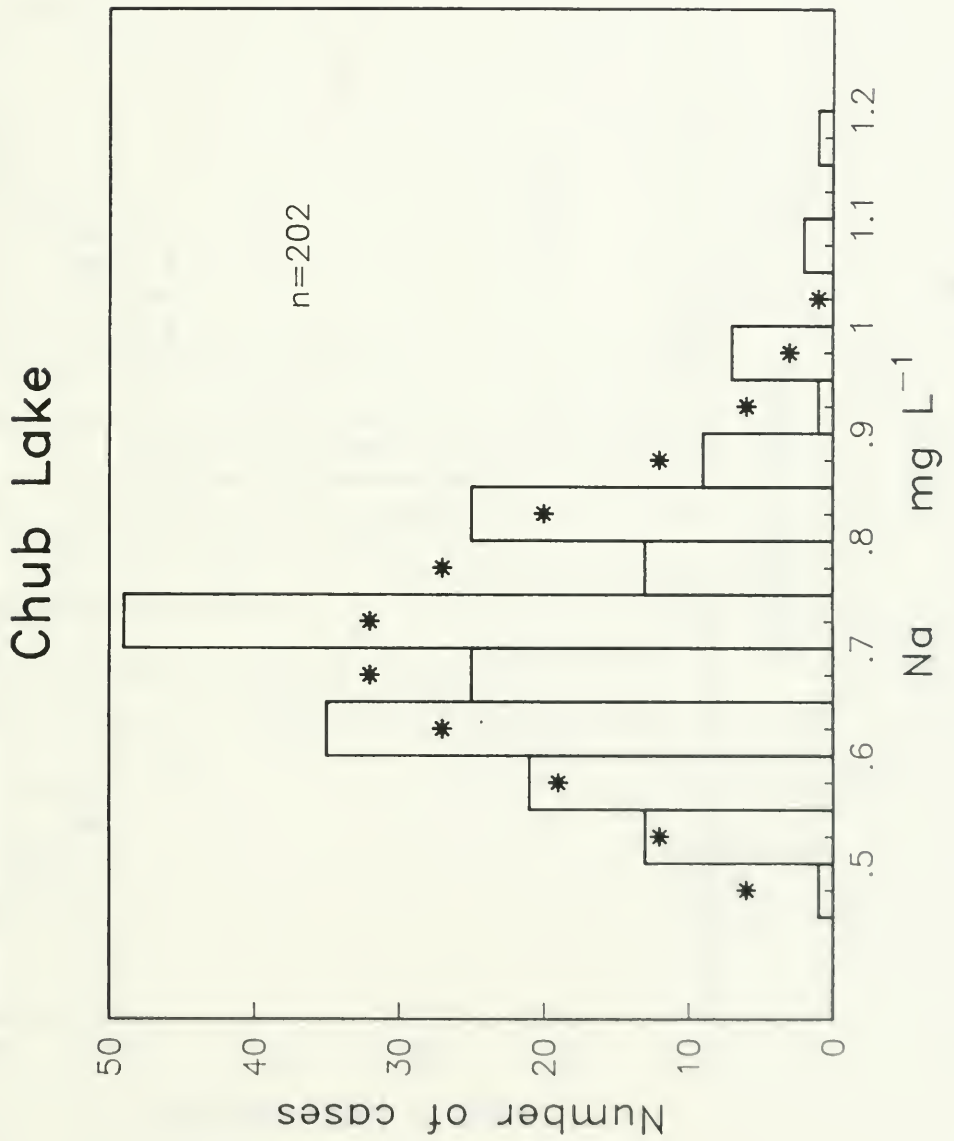

Chub Lake
n=197
Number of cases
0
10
20
30
40
.52
.56
.6
.64
.68
.72
.76
.8
.84
.88
Mg mg L^{-1}

Fig. 5.f


Chub Lake
n=202
Number of cases
0
10
20
30
40
50
.5
.6
.7
.8
.9
1
1.1
1.2
Na mg L^{-1}

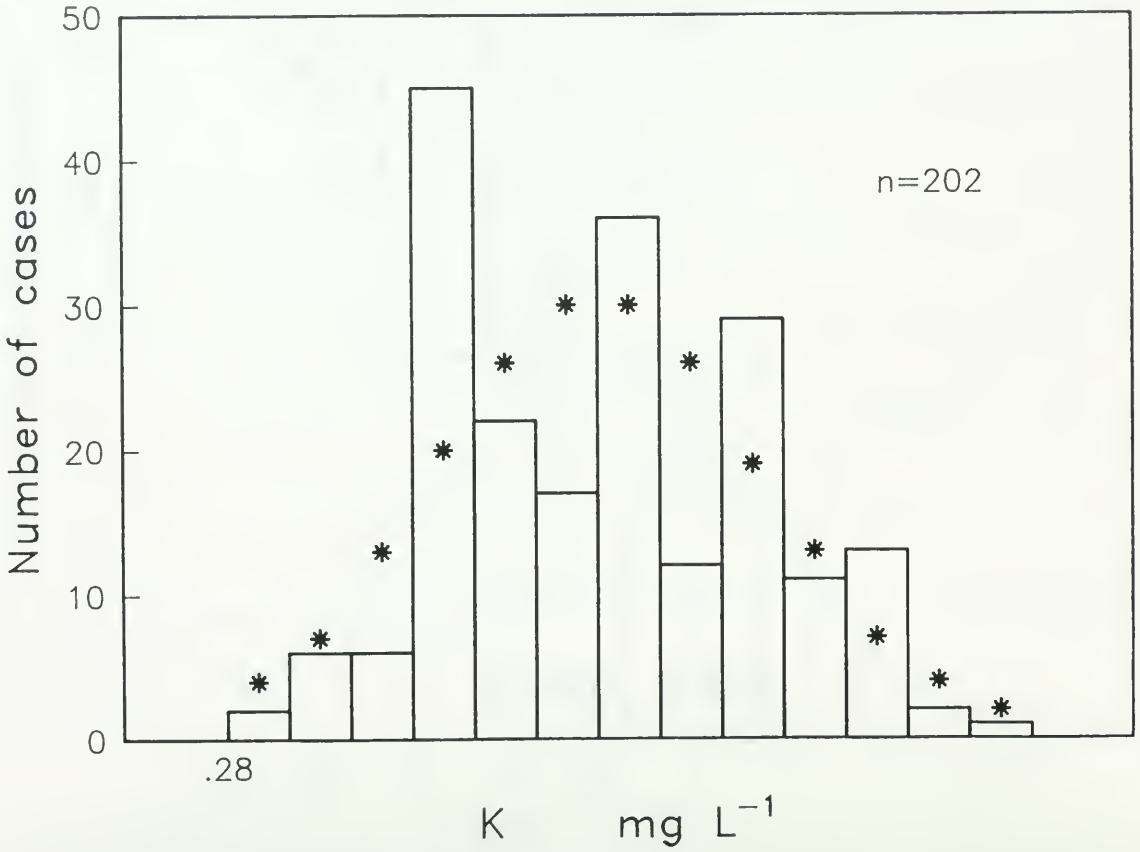


Fig. 5.g

Fig. 5.h

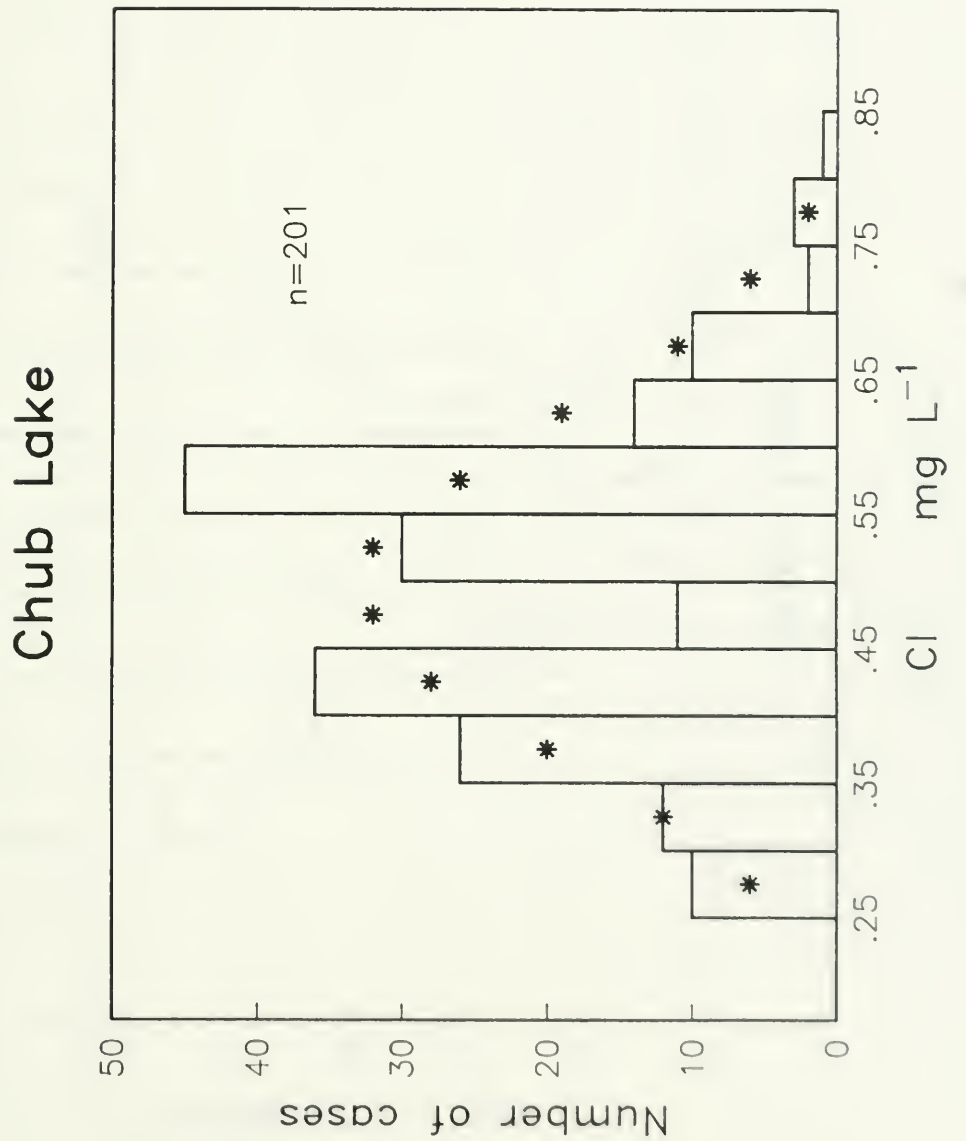

Chub Lake
n=201
Number of cases
0
10
20
30
40
50
.25
.35
.45
.55
.65
.75
.85
Cl mg L^{-1}

Fig. 5.i

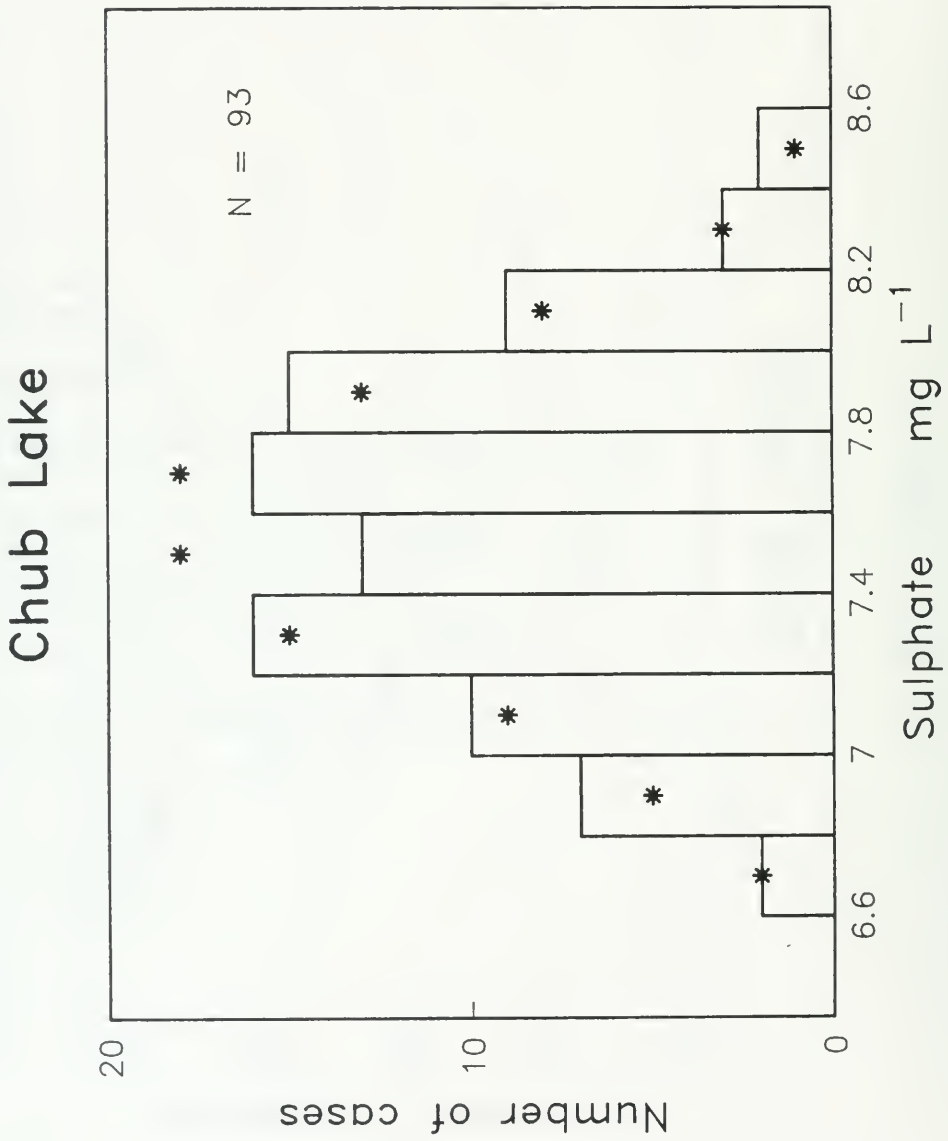

Chub Lake
N = 93
Number of cases
0
10
20
6.6
7
7.4
7.8
8.2
8.6
Sulphate mg L^{-1}

Fig. 5.j

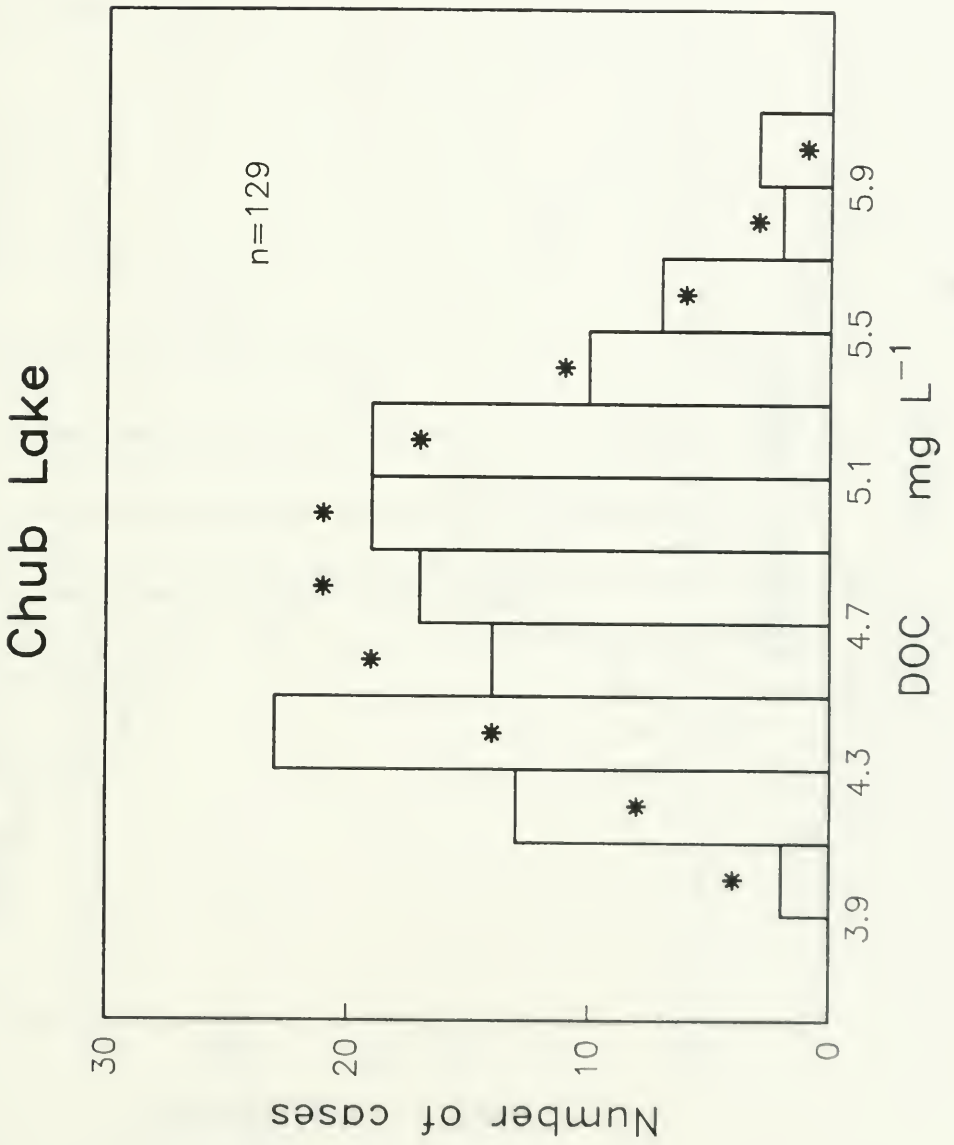

Chub Lake
n=129
Number of cases
0
10
20
30
3.9
4.3
4.7
5.1
5.5
5.9
DOC mg L^{-1}

Fig. 5.k

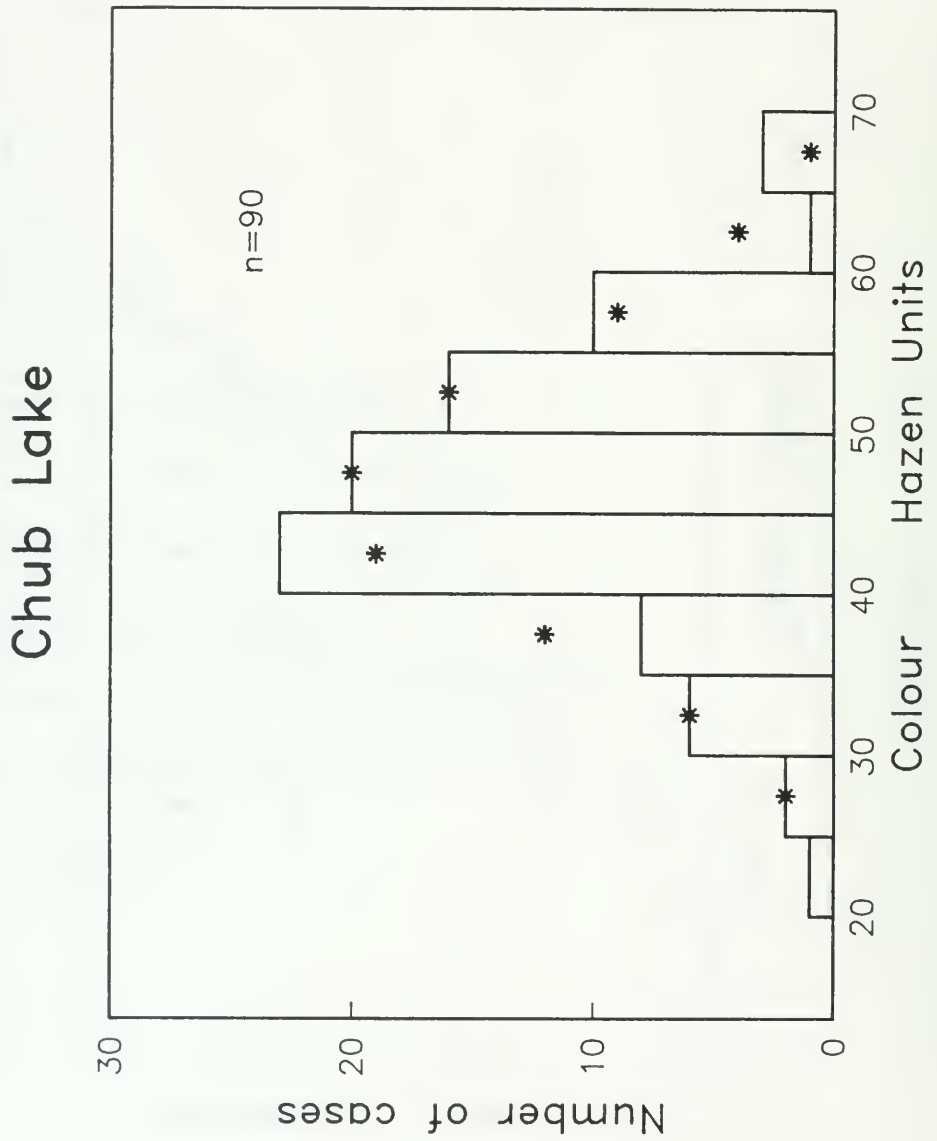

Chub Lake
n=90
Number of cases
0
10
20
30
20
30
40
50
60
70
Colour Hazen Units

Fig. 5.1

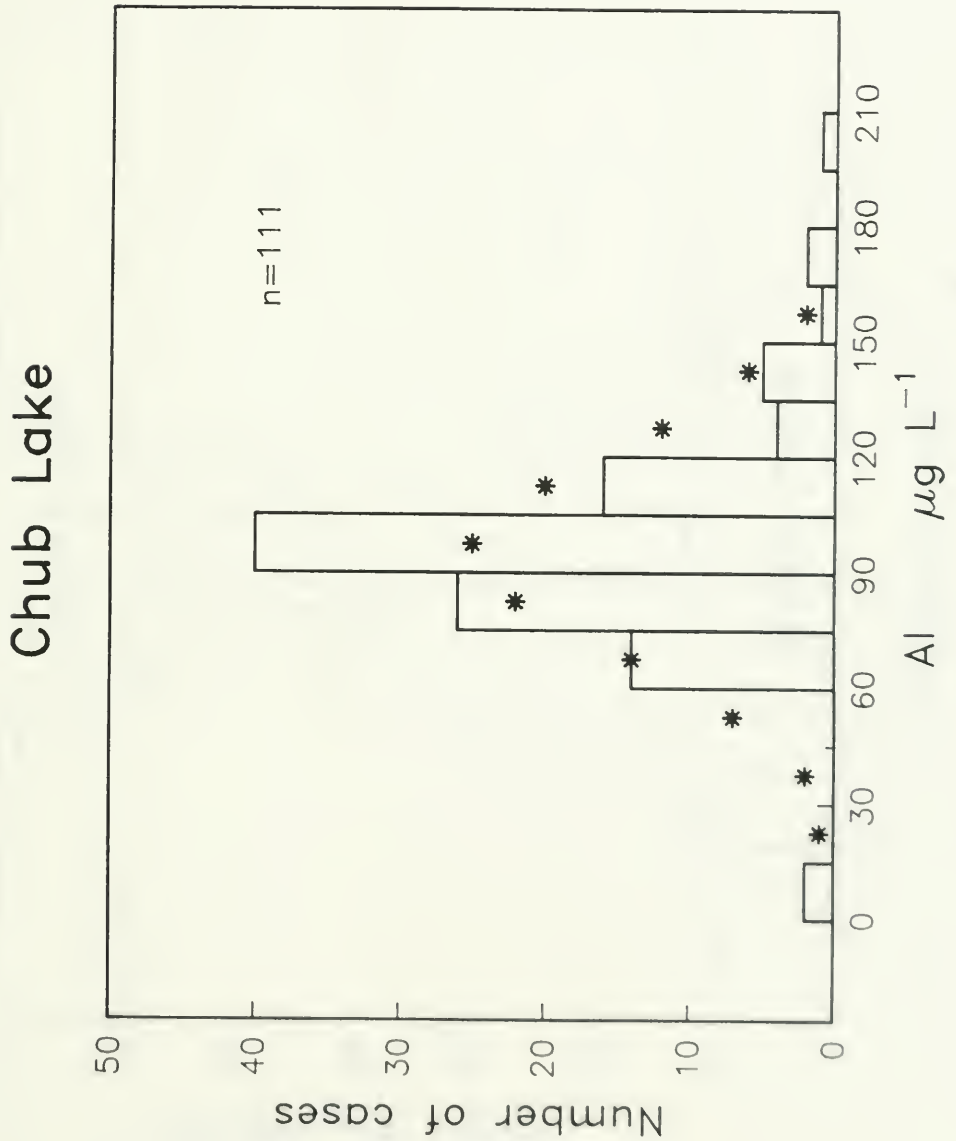

Chub Lake
n=111
Number of cases
0
10
20
30
40
50
0
30
60
90
120
150
180
210
Al μg L⁻¹

Fig. 6.a

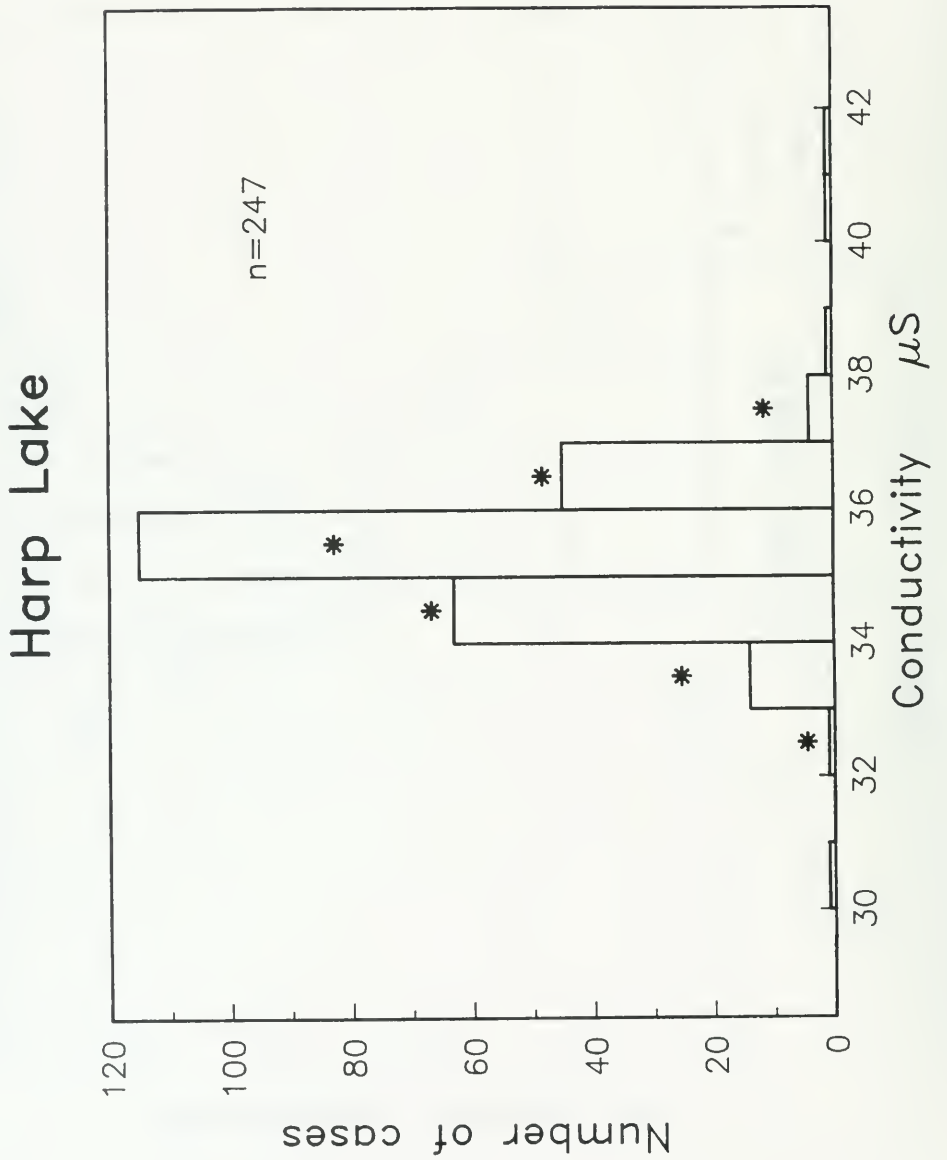

Harp Lake
n=247
Number of cases
0
20
40
60
80
100
120
30
32
34
36
38
40
42
Conductivity µS

Fig. 6.b

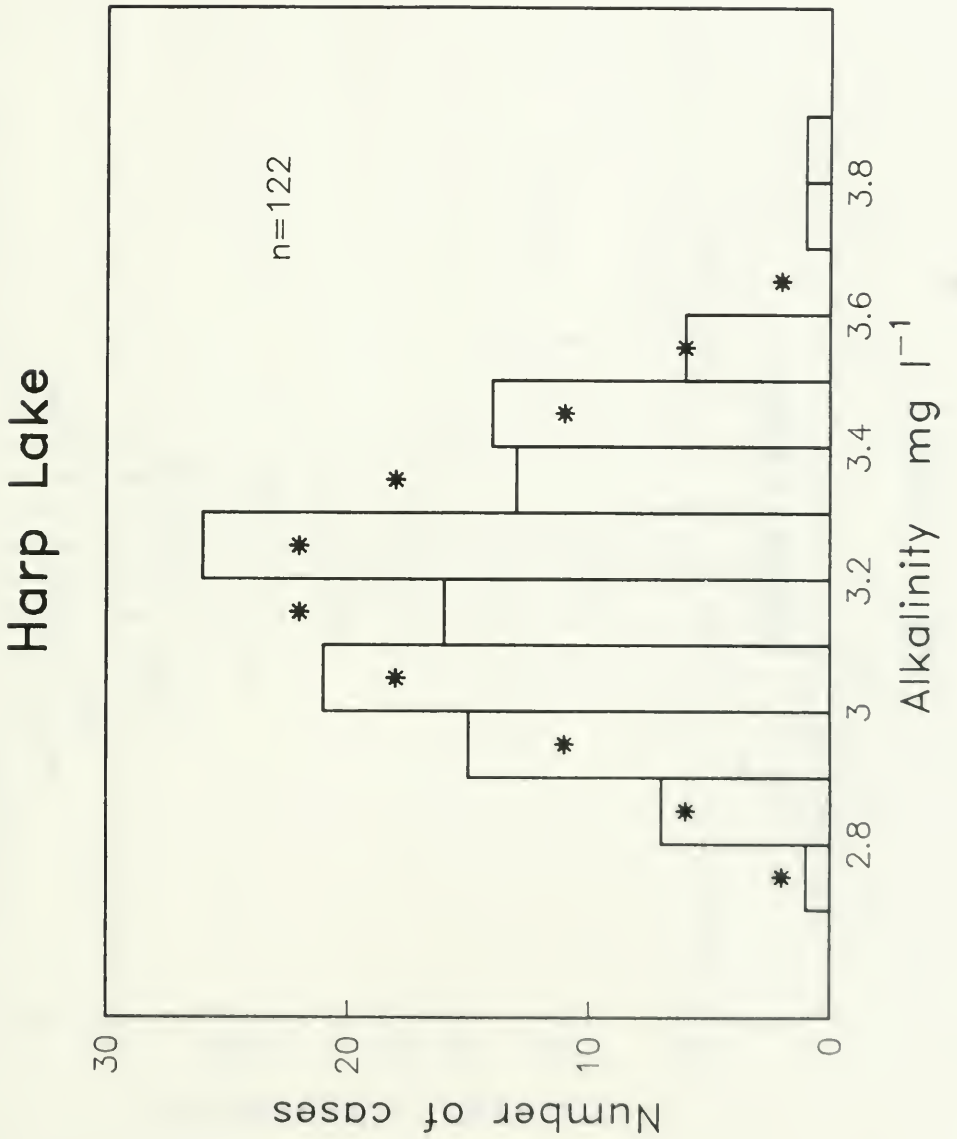

Harp Lake
n=122
Number of cases
0
10
20
30
2.8
3
3.2
3.4
3.6
3.8
Alkalinity mg l^{-1}

Fig. 6.c

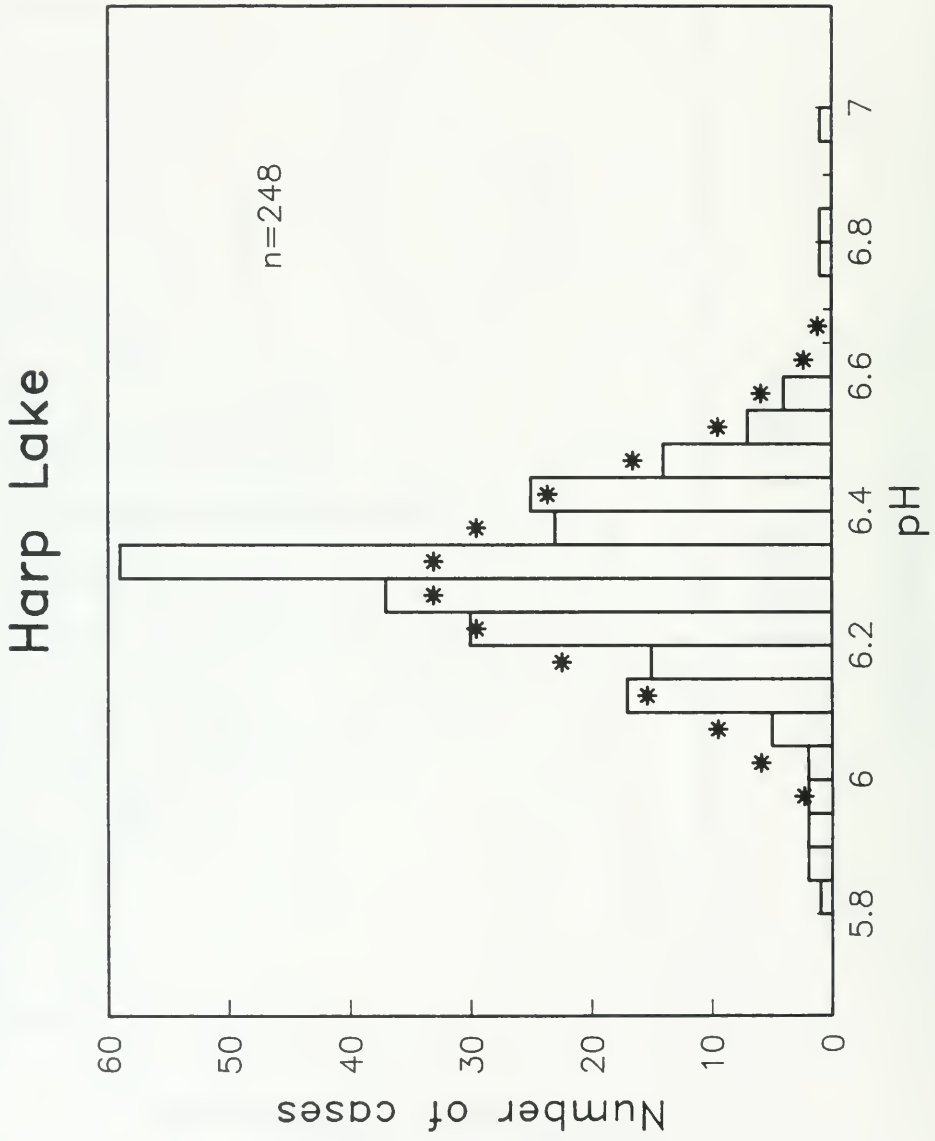

Harp Lake
n=248
Number of cases
0
10
20
30
40
50
60
5.8
6
6.2
6.4
6.6
6.8
7
pH

Fig. 6.d

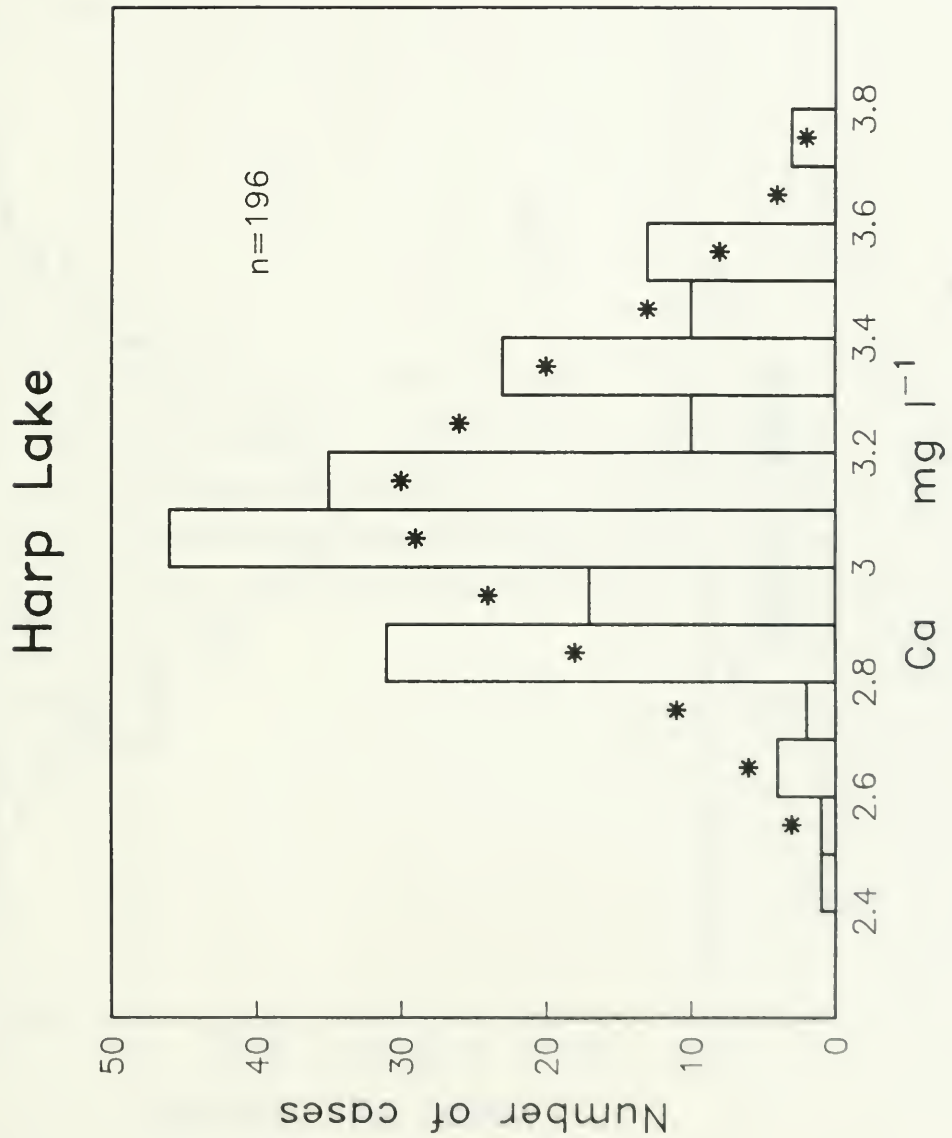

Harp Lake
n=196
Number of cases
0
10
20
30
40
50
2.4
2.6
2.8
3
3.2
3.4
3.6
3.8
Ca mg l⁻¹

Fig. 6.e

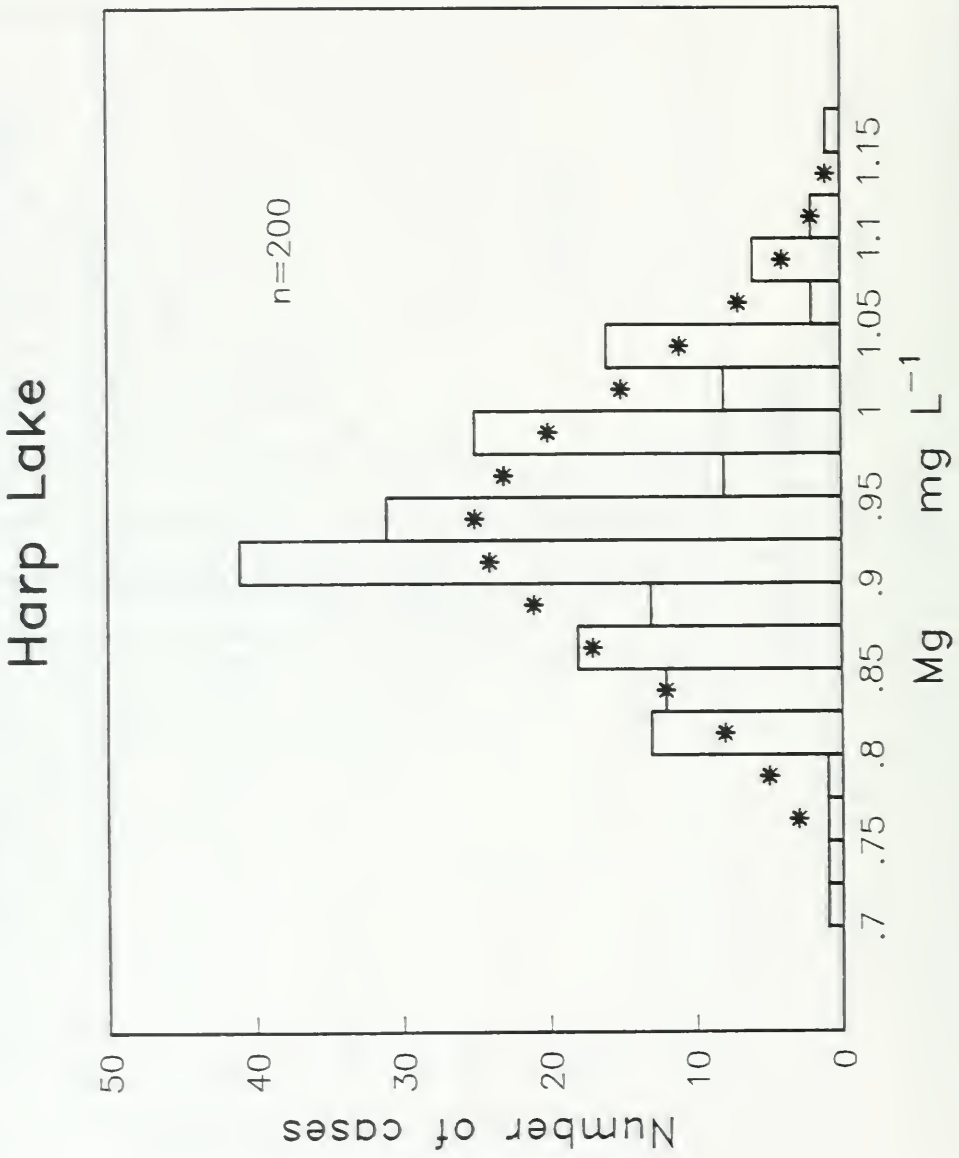

Harp Lake
n=200
Number of cases
0
10
20
30
40
50
.7
.75
.8
.85
.9
.95
1
1.05
1.1
1.15
Mg mg L^{-1}

Fig. 6.f

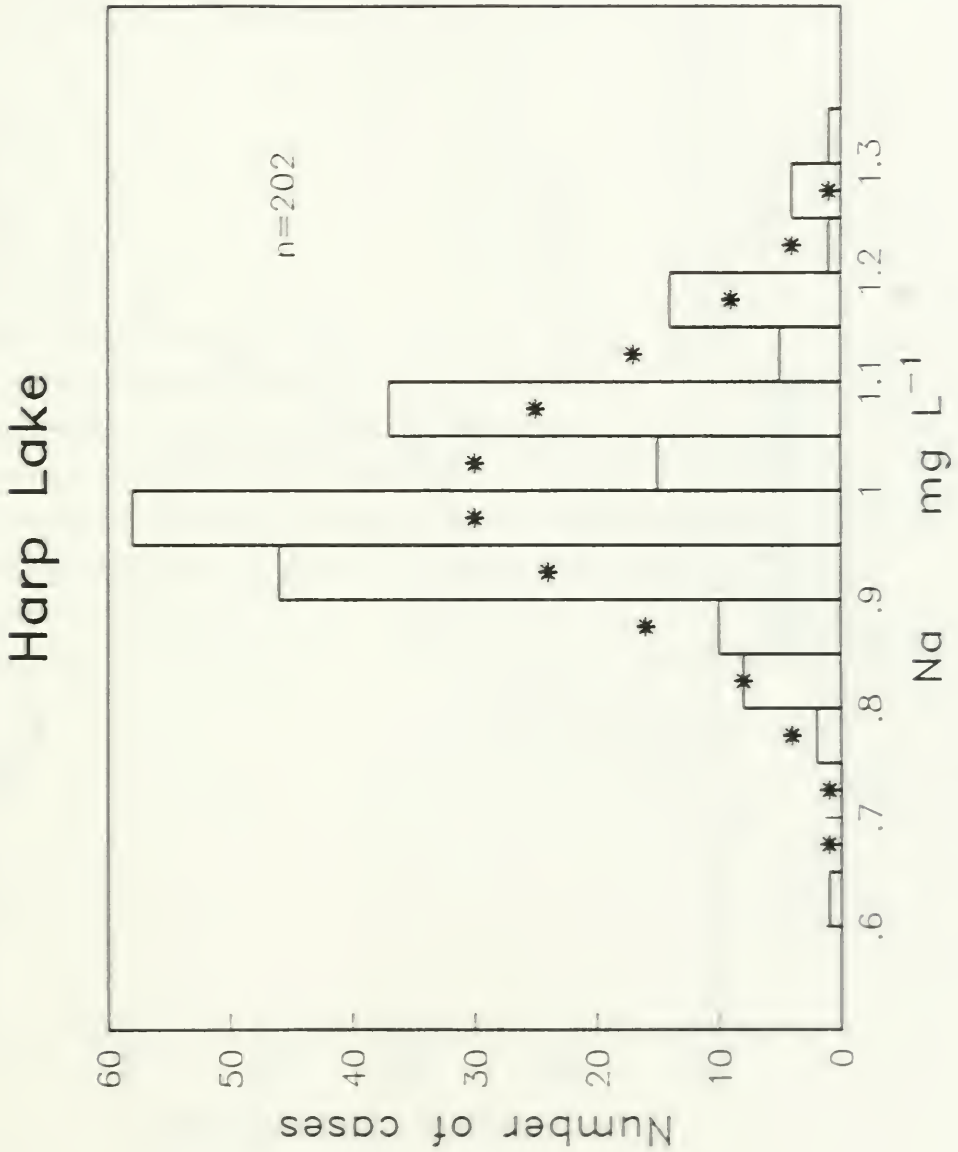

Harp Lake
n=202
Number of cases
0
10
20
30
40
50
60
.6
.7
.8
.9
1
1.1
1.2
1.3
Na mg L⁻¹

Fig. 6.g

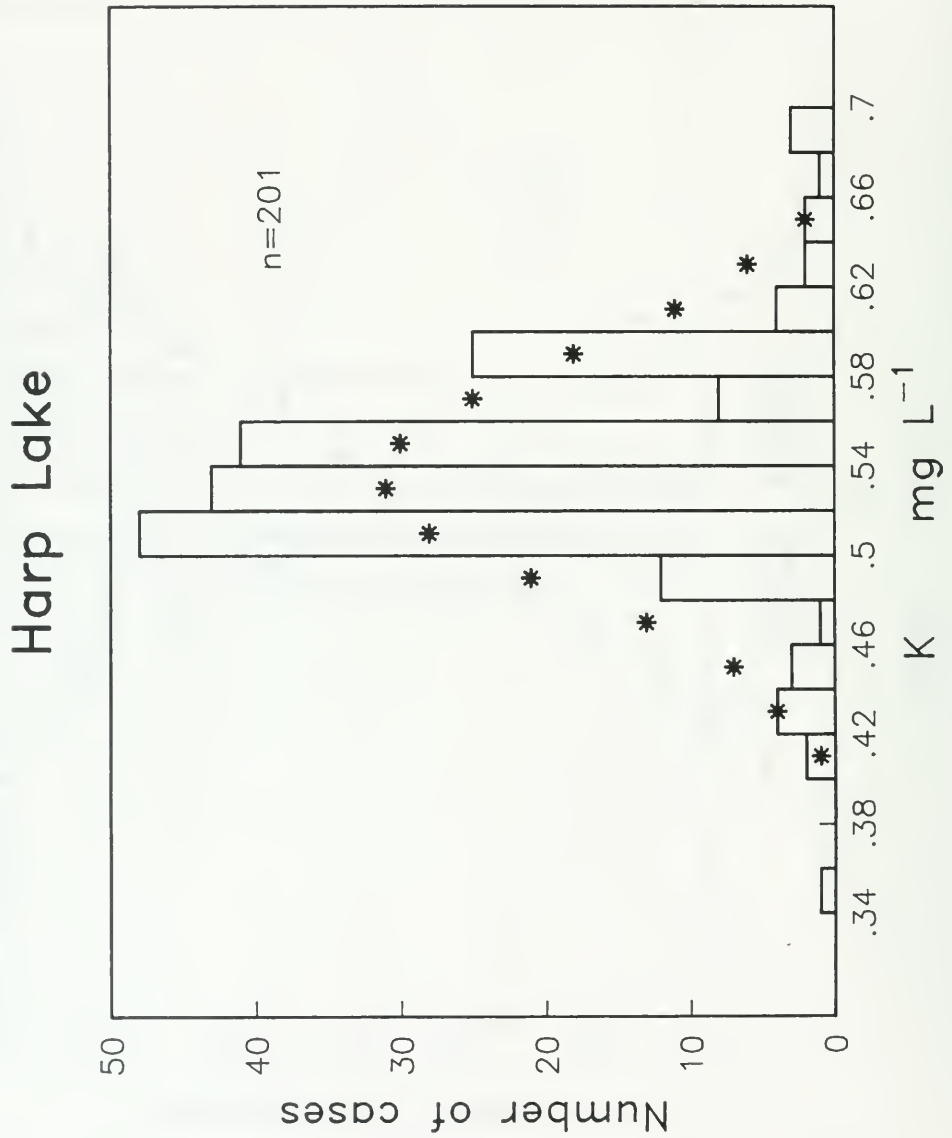

Harp Lake
n=201
Number of cases
0
10
20
30
40
50
.34
.38
.42
.46
.5
.54
.58
.62
.66
.7
K mg L^{-1}

Fig. 6.h

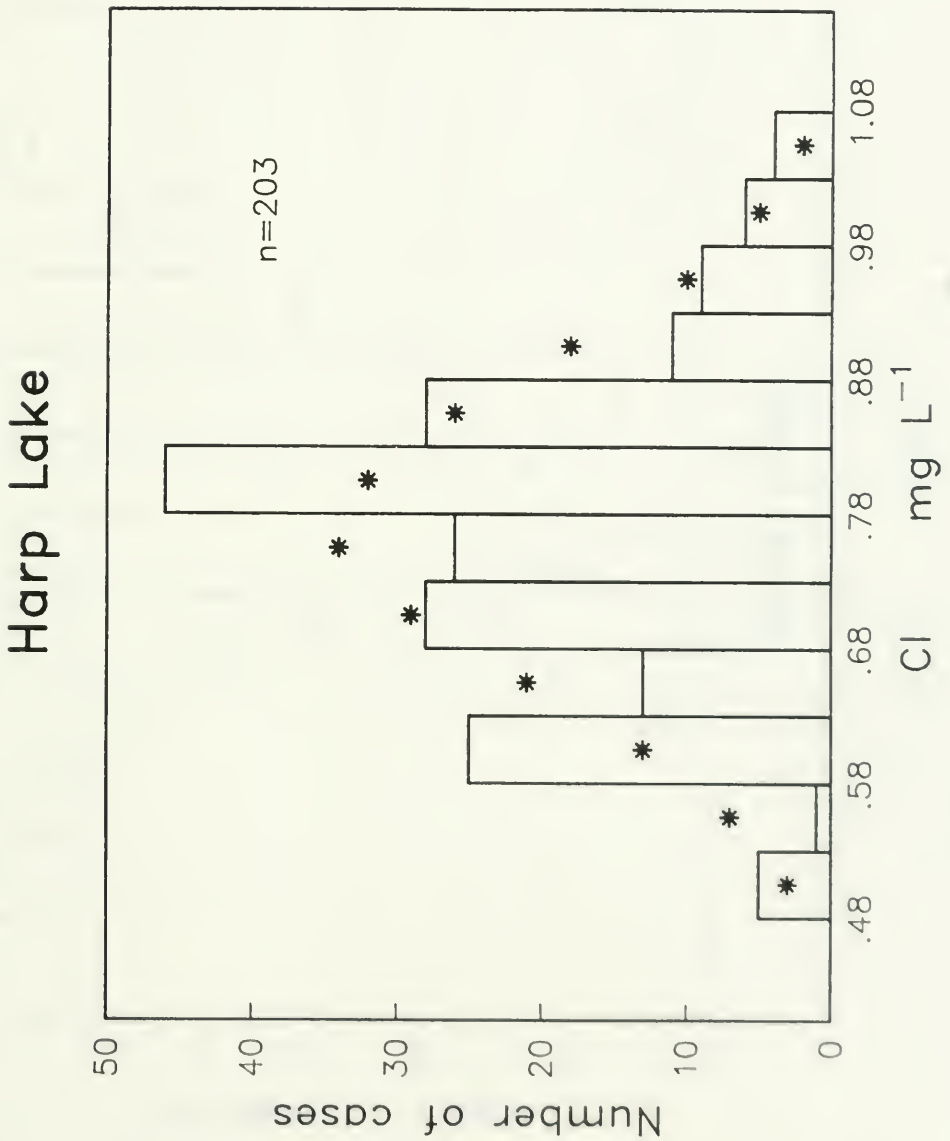

Harp Lake
n=203
Number of cases
0
10
20
30
40
50
.48
.58
.68
.78
.88
.98
1.08
Cl mg L^{-1}

Fig. 6.i

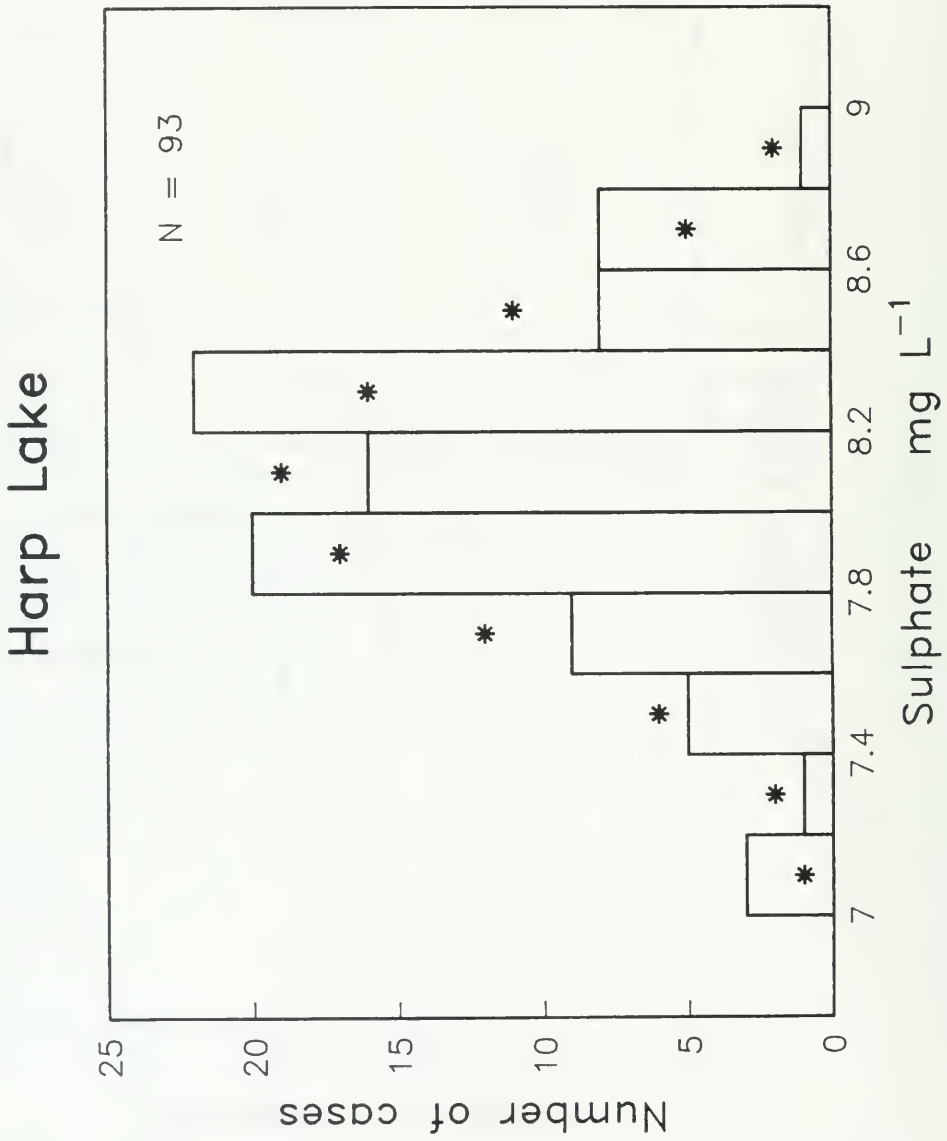

Harp Lake
N = 93
Number of cases
0
5
10
15
20
25
7
7.4
7.8
8.2
8.6
9
Sulphate mg L^{-1}

Fig. 6.j

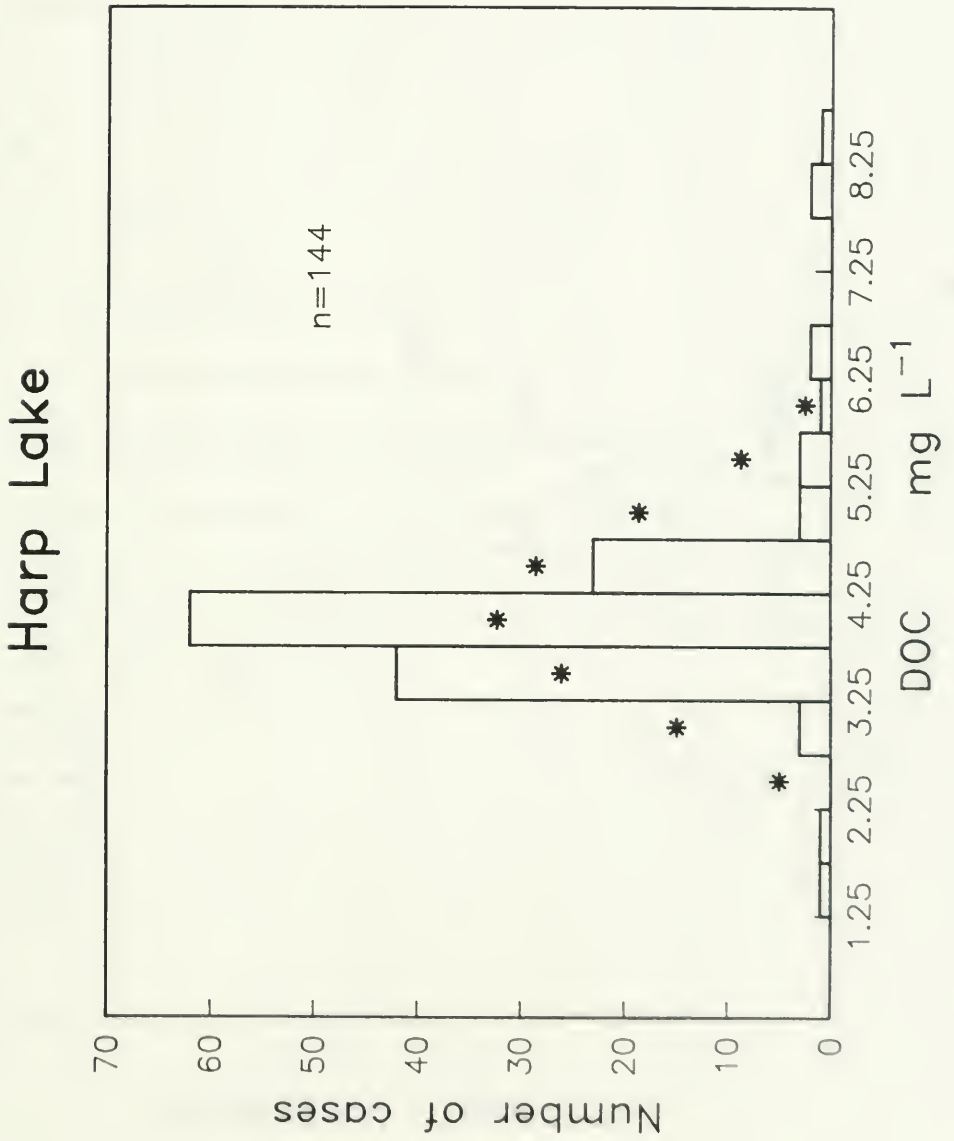

Harp Lake
n=144
Number of cases
0
10
20
30
40
50
60
70
1.25
2.25
3.25
4.25
5.25
6.25
7.25
8.25
DOC mg L^{-1}

Fig. 6.k

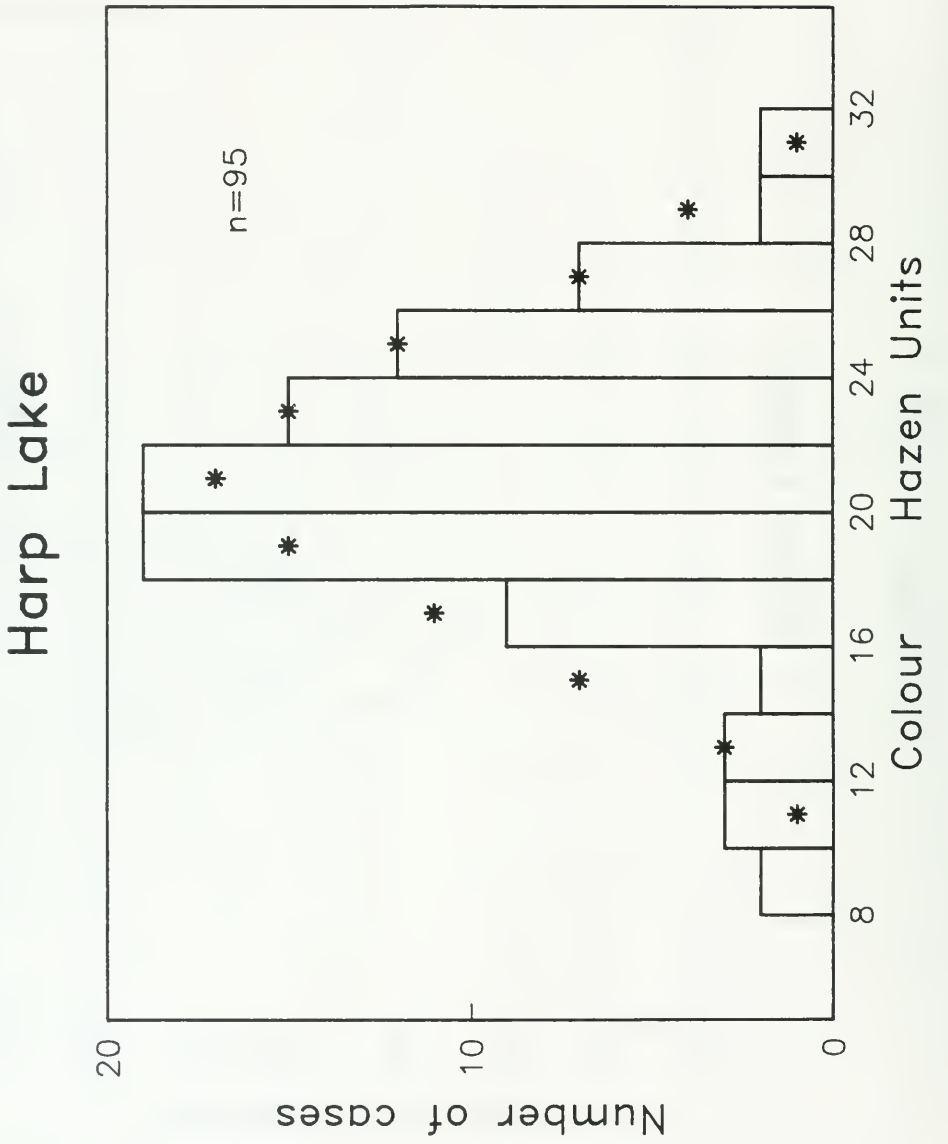

Harp Lake
n=95
Number of cases
0
10
20
8
12
16
20
24
28
32
Colour Hazen Units

Fig. 6.1

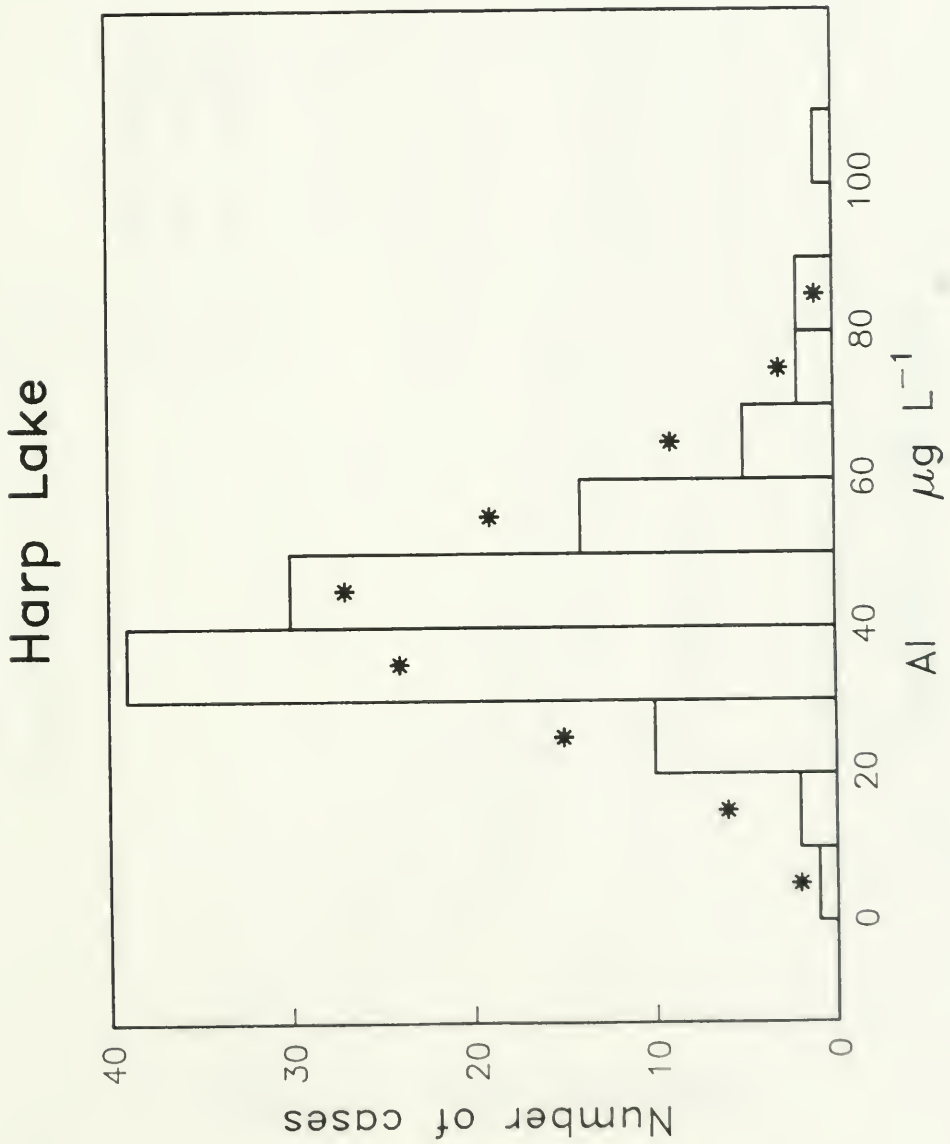


Fig. 7.a

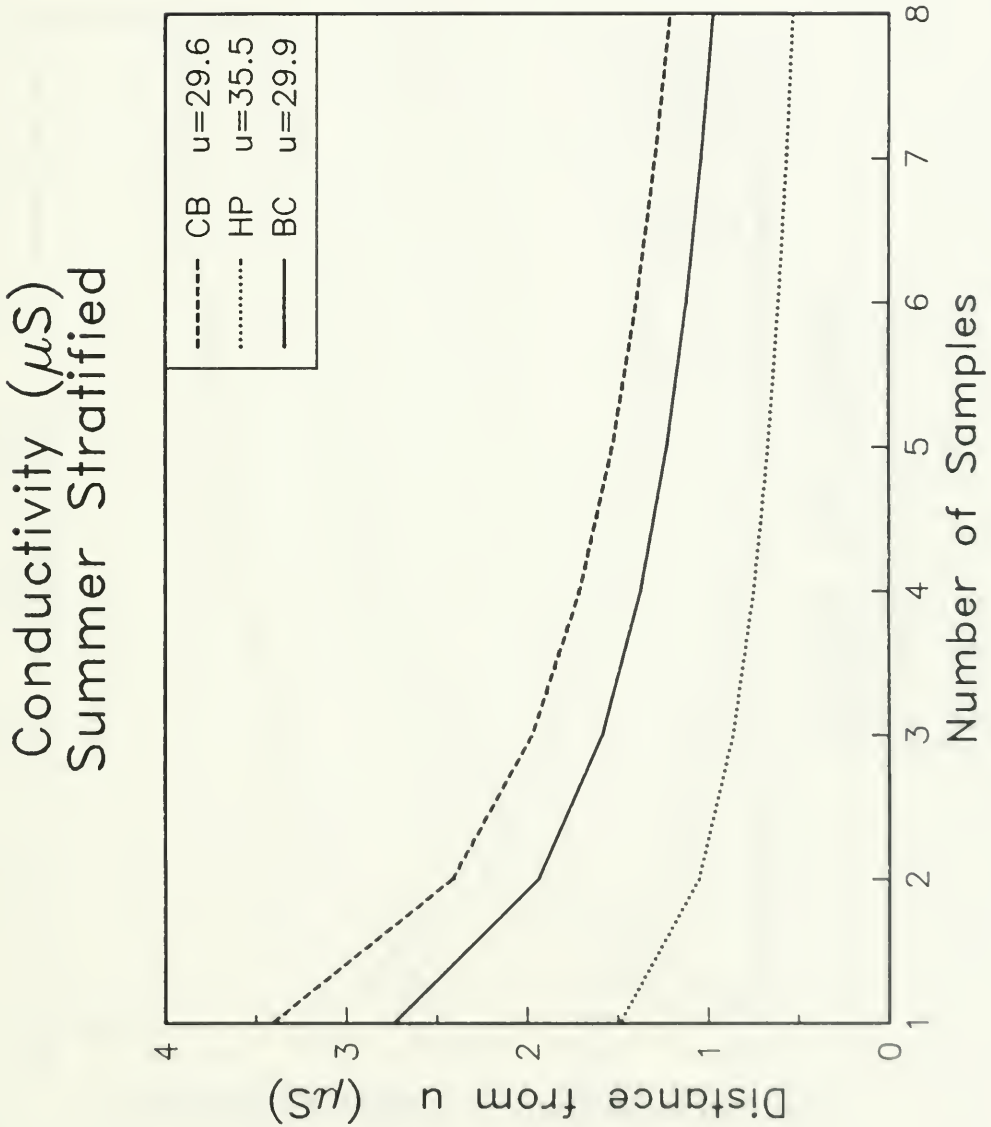

Conductivity (μS)
Summer Stratified
CB u=29.6
HP u=35.5
BC u=29.9
Distance from u (μS)
Number of Samples
0
1
2
3
4
1
2
3
4
5
6
7
8

Fig. 7.b

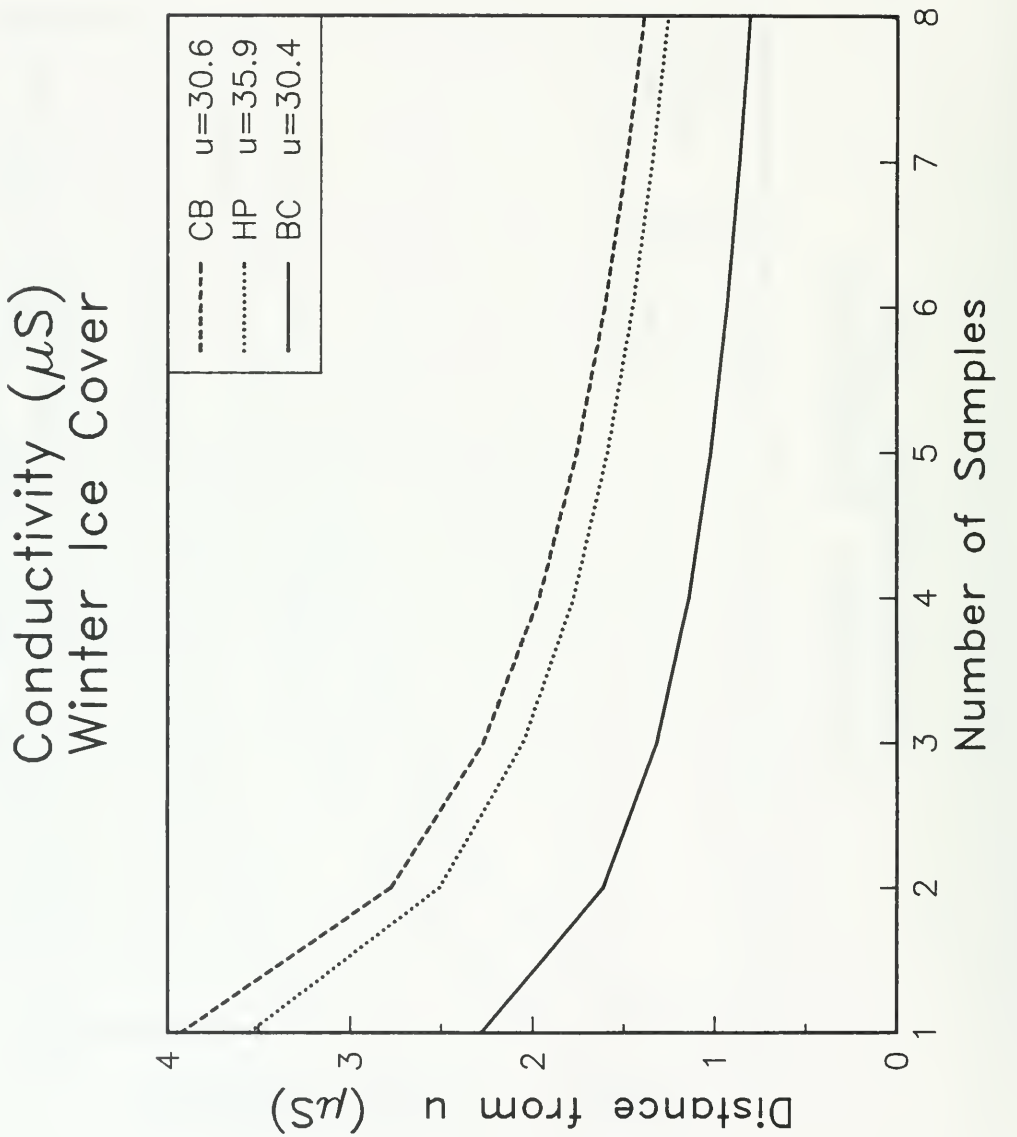

Conductivity (μS)
Winter Ice Cover
CB u=30.6
HP u=35.9
BC u=30.4
Distance from u (μS)
Number of Samples
0
1
2
3
4
1
2
3
4
5
6
7
8

Fig. 7.c

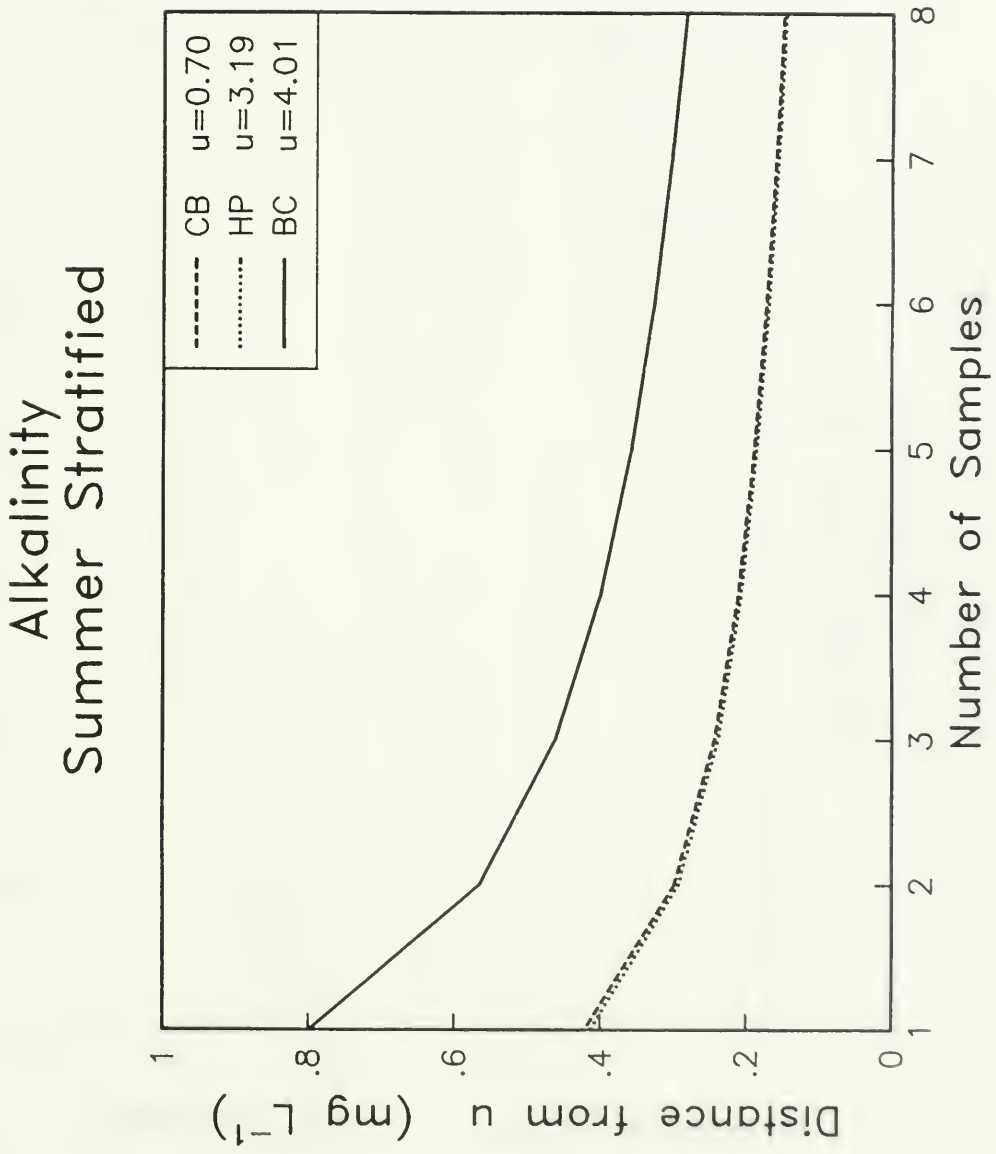

Alkalinity
Summer Stratified
CB u=0.70
HP u=3.19
BC u=4.01
Distance from u (mg L⁻¹)
Number of Samples
0
.2
.4
.6
.8
1
1
2
3
4
5
6
7
8

Fig. 7.d

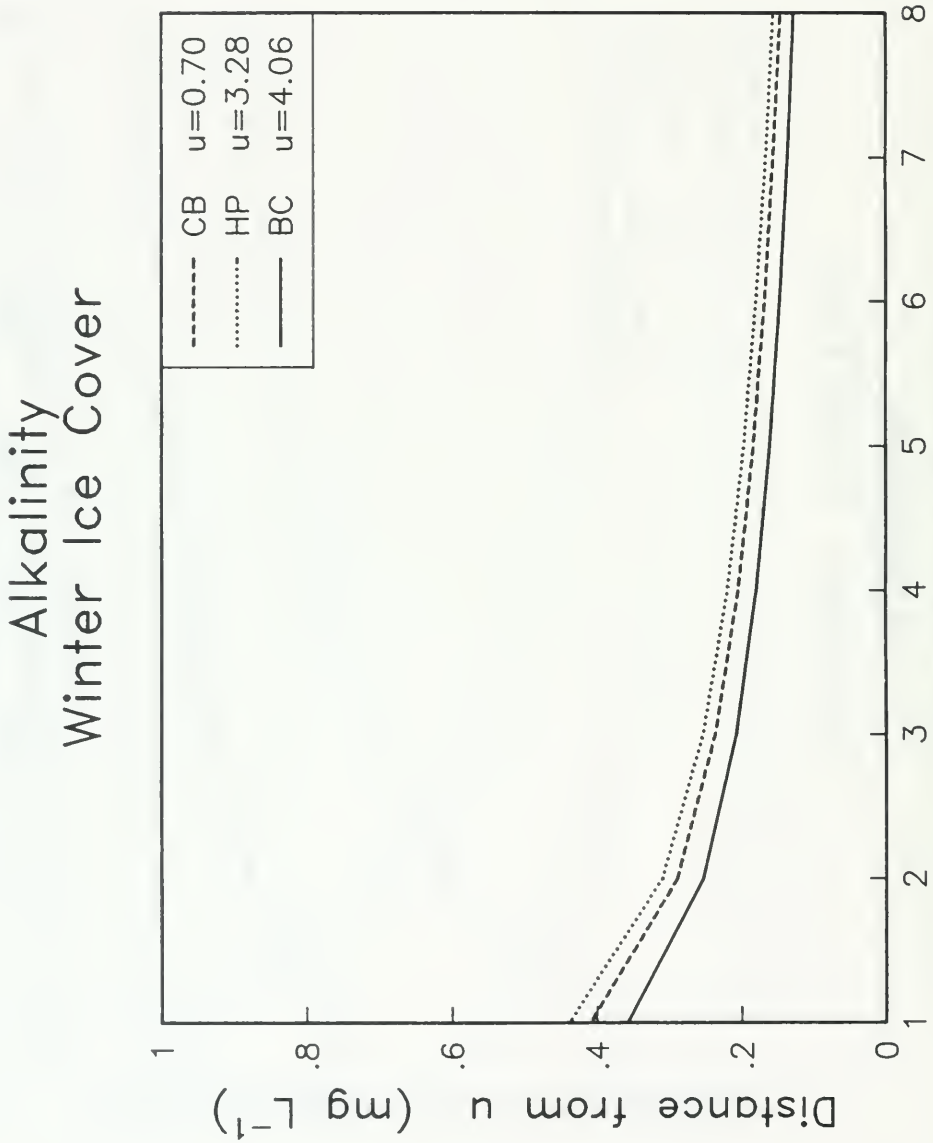

Alkalinity
Winter Ice Cover
CB u=0.70
HP u=3.28
BC u=4.06
Distance from u (mg L⁻¹)
Number of Samples
0
.2
.4
.6
.8
1
1
2
3
4
5
6
7
8

Fig. 7.e

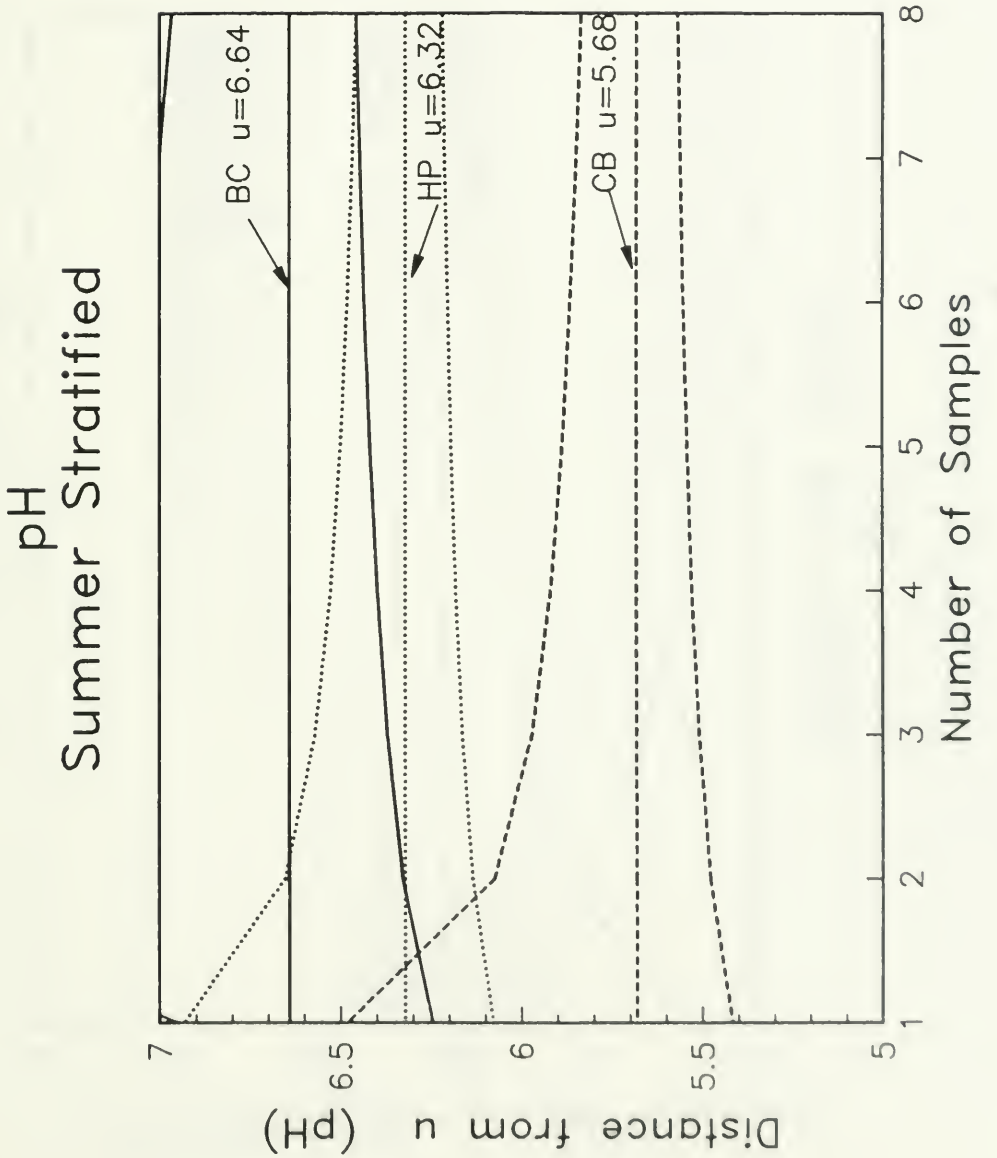

pH
Summer Stratified
BC u=6.64
HP u=6.32
CB u=5.68
Distance from u (pH)
7
6.5
6
5.5
5
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.f

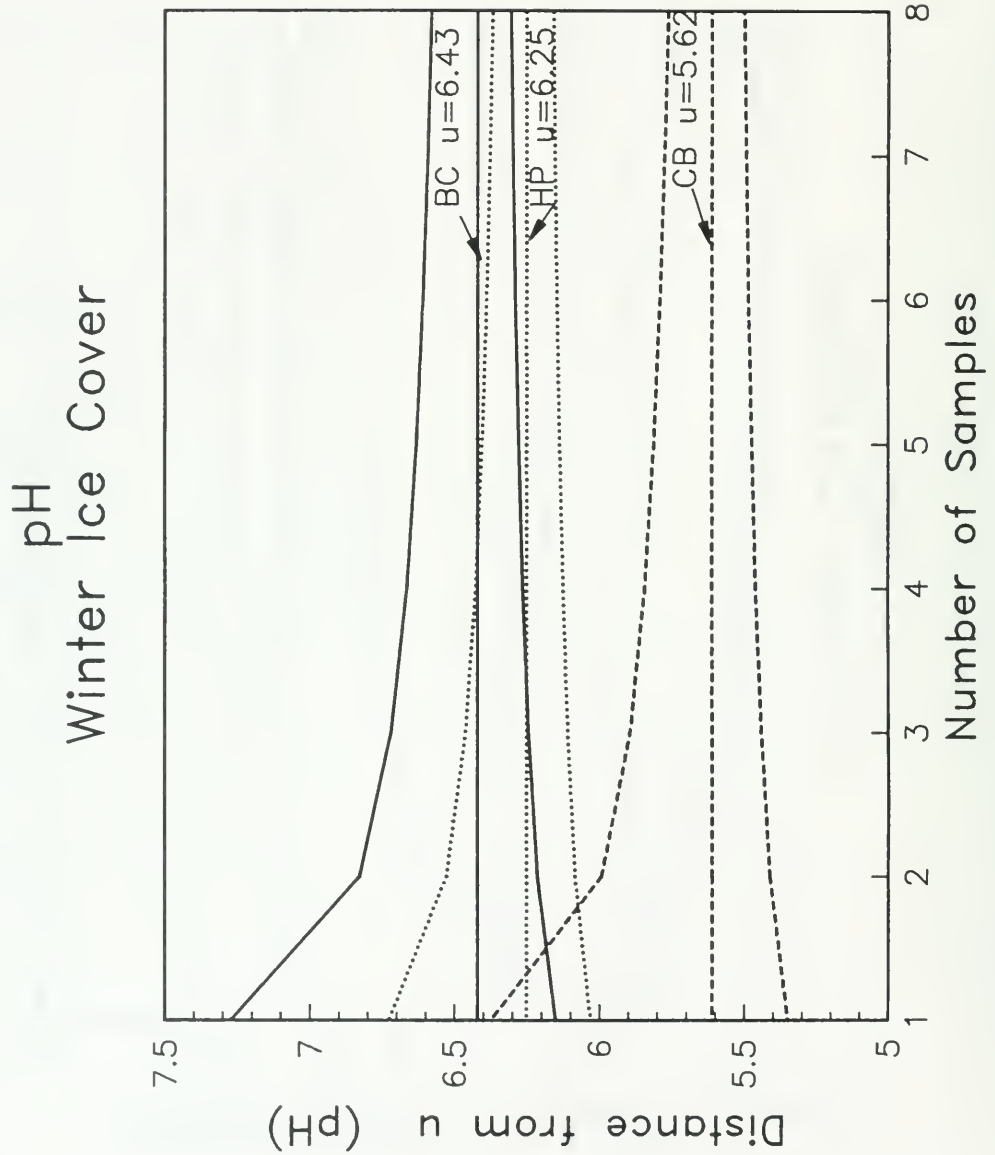

pH
Winter Ice Cover
Distance from u (pH)
Number of Samples
BC u=6.43
HP u=6.25
CB u=5.62
7.5
7
6.5
6
5.5
5
1
2
3
4
5
6
7
8

Fig. 7.g

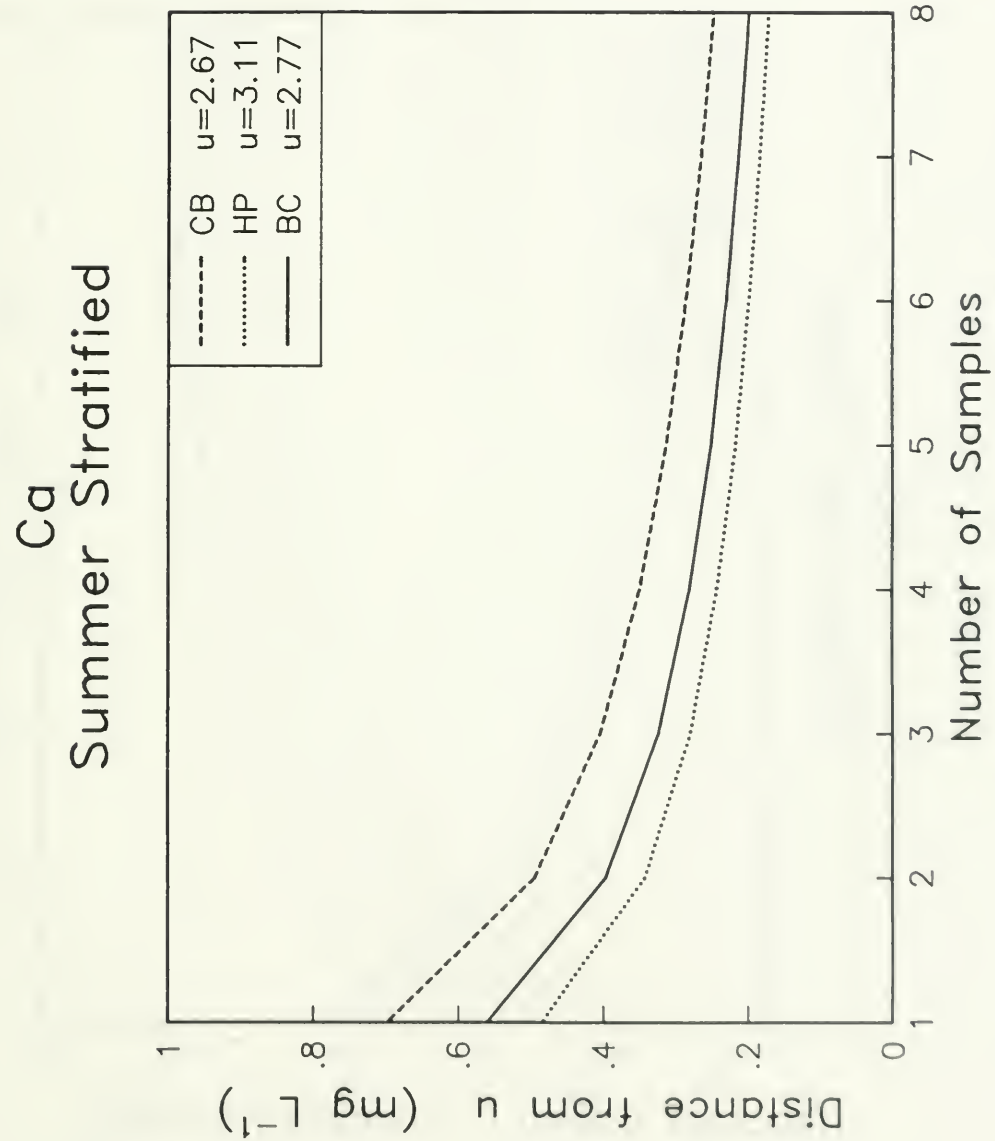

Ca
Summer Stratified
CB u=2.67
HP u=3.11
BC u=2.77
Distance from u (mg L⁻¹)
Number of Samples
0
.2
.4
.6
.8
1
1
2
3
4
5
6
7
8

Fig. 7.h

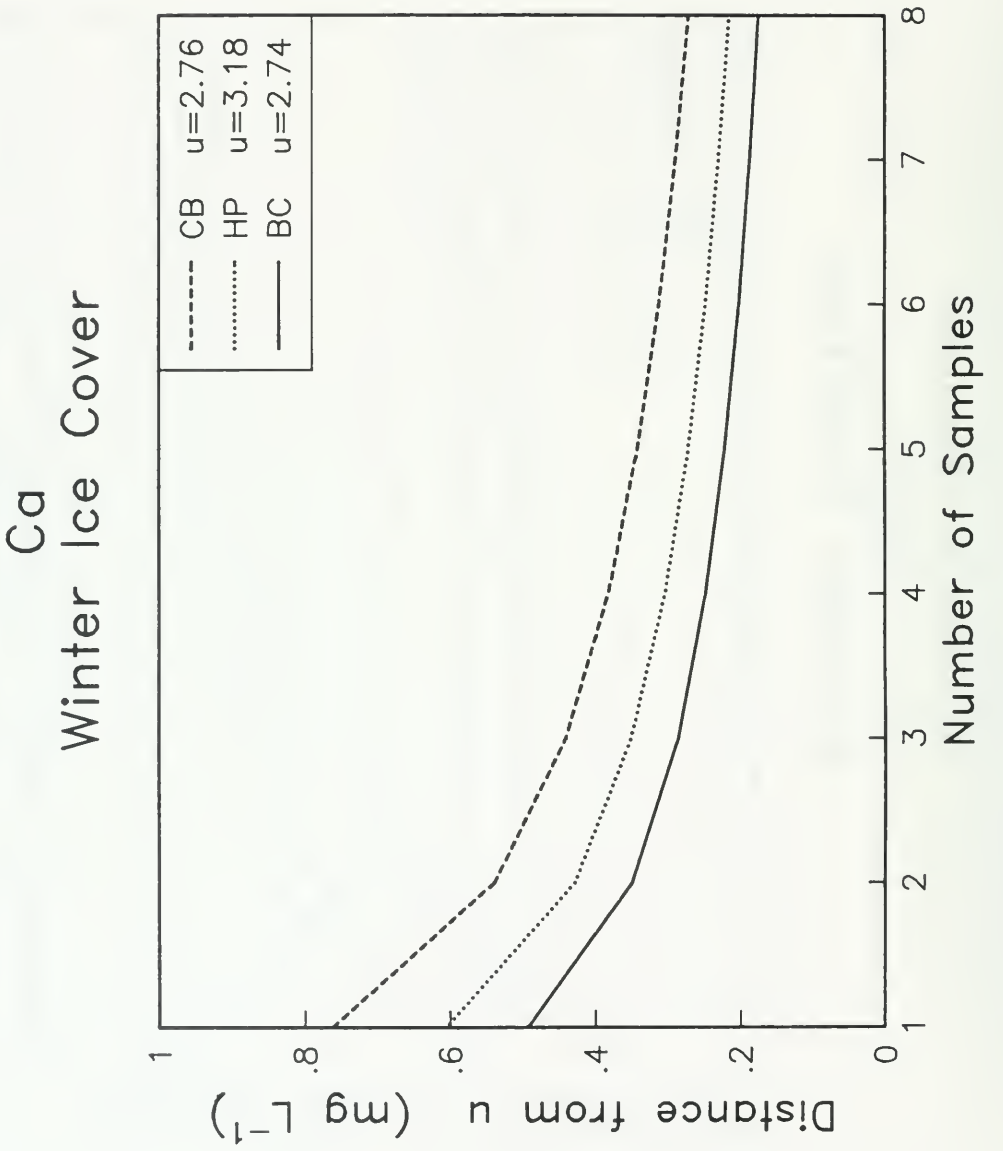

Ca
Winter Ice Cover
CB u=2.76
HP u=3.18
BC u=2.74
Distance from u (mg L⁻¹)
Number of Samples
0
.2
.4
.6
.8
1
1
2
3
4
5
6
7
8

Fig. 7.i

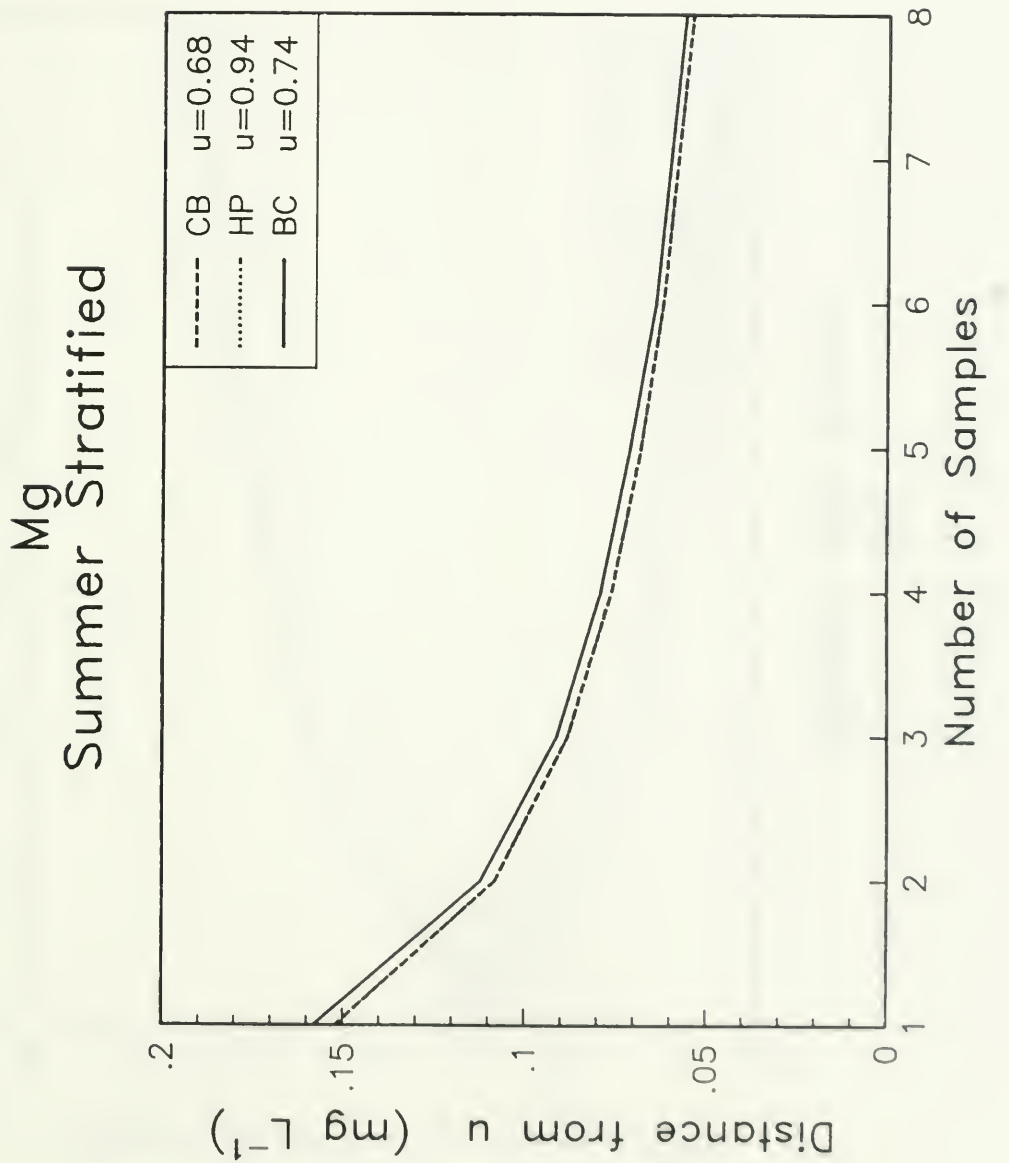

Mg
Summer Stratified
CB u=0.68
HP u=0.94
BC u=0.74
Distance from u (mg L⁻¹)
.2
.15
.1
.05
0
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.j

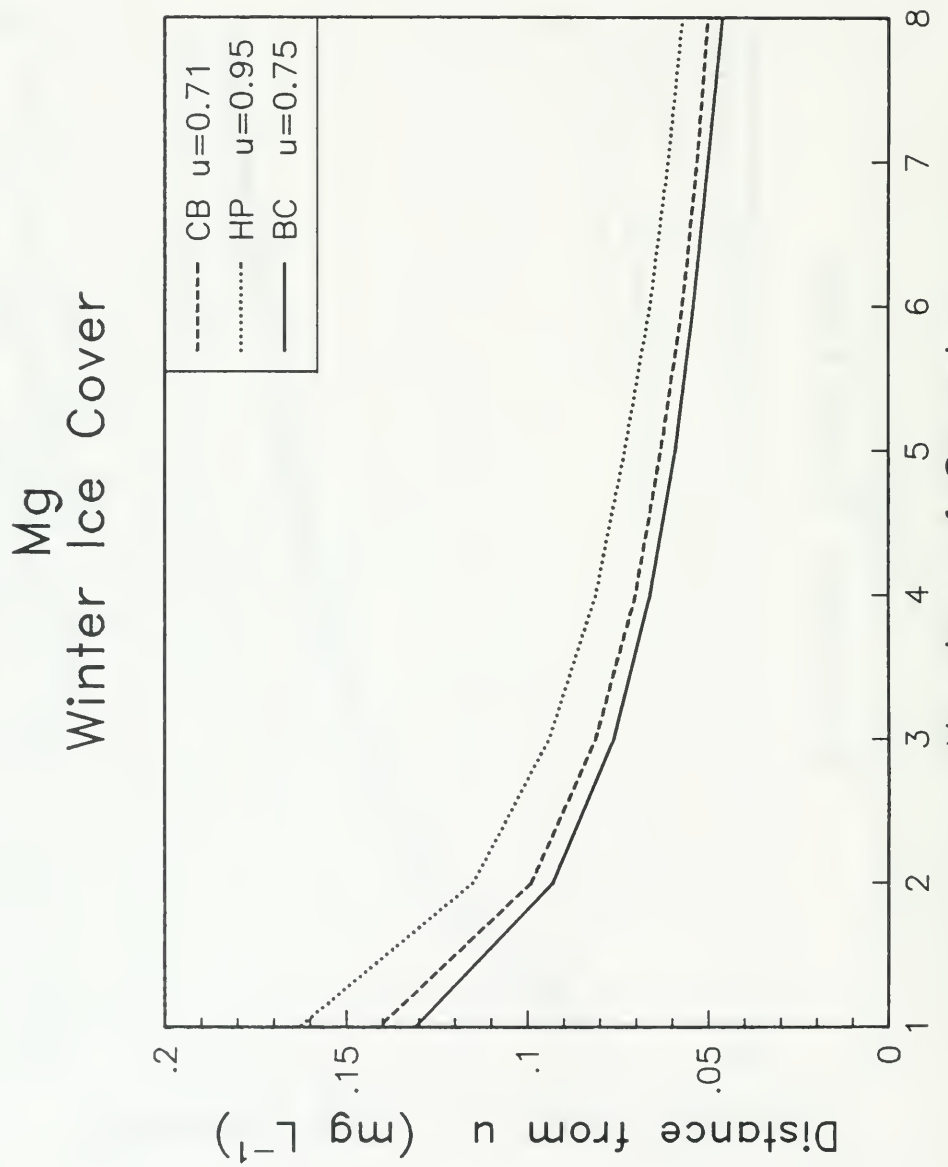

Mg
Winter Ice Cover
CB u=0.71
HP u=0.95
BC u=0.75
Distance from u (mg L⁻¹)
0
.05
.1
.15
.2
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.k

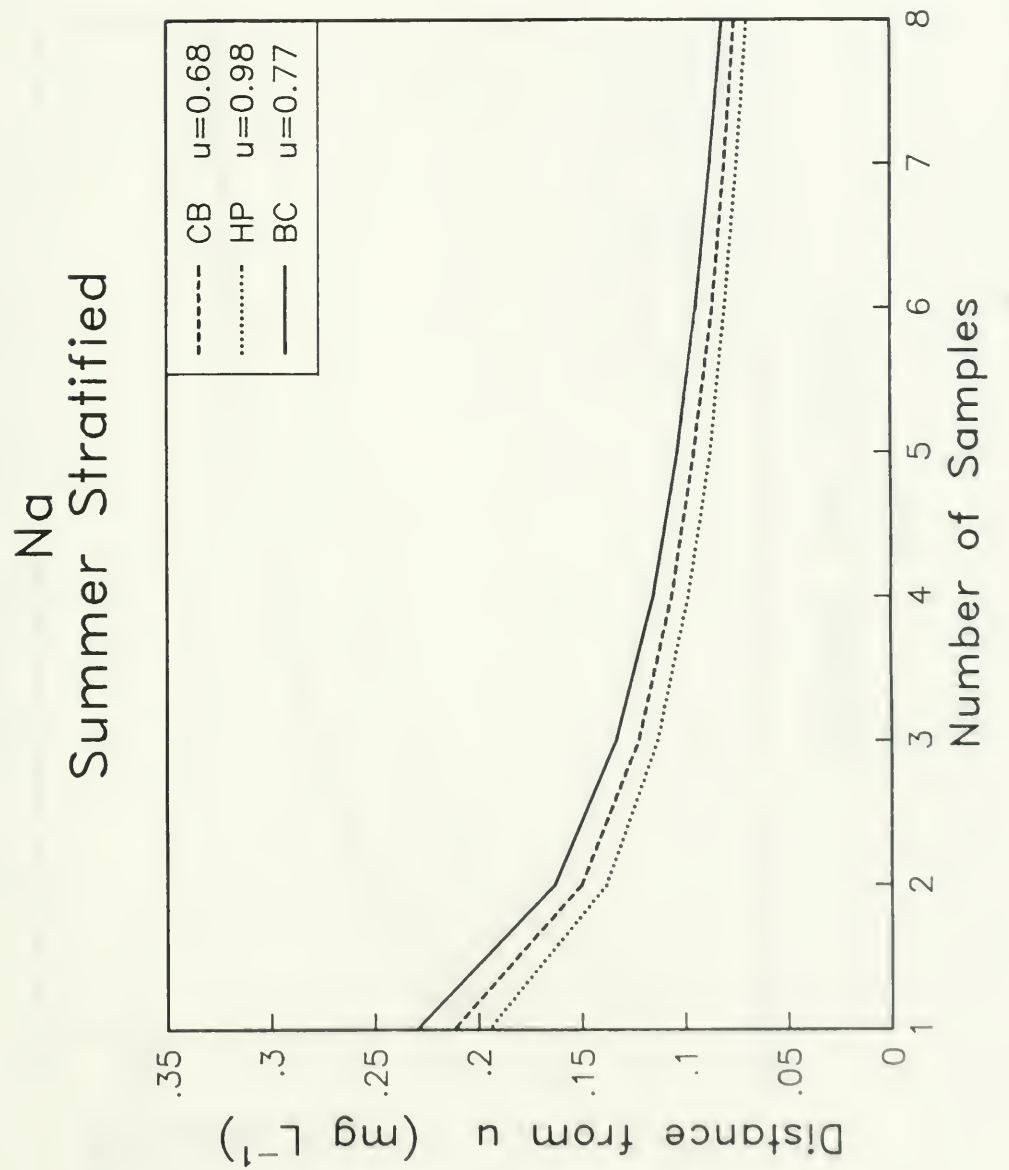

Na
Summer Stratified
CB u=0.68
HP u=0.98
BC u=0.77
Distance from u (mg L⁻¹)
Number of Samples
.35
.3
.25
.2
.15
.1
.05
0
1
2
3
4
5
6
7
8

Fig. 7.1

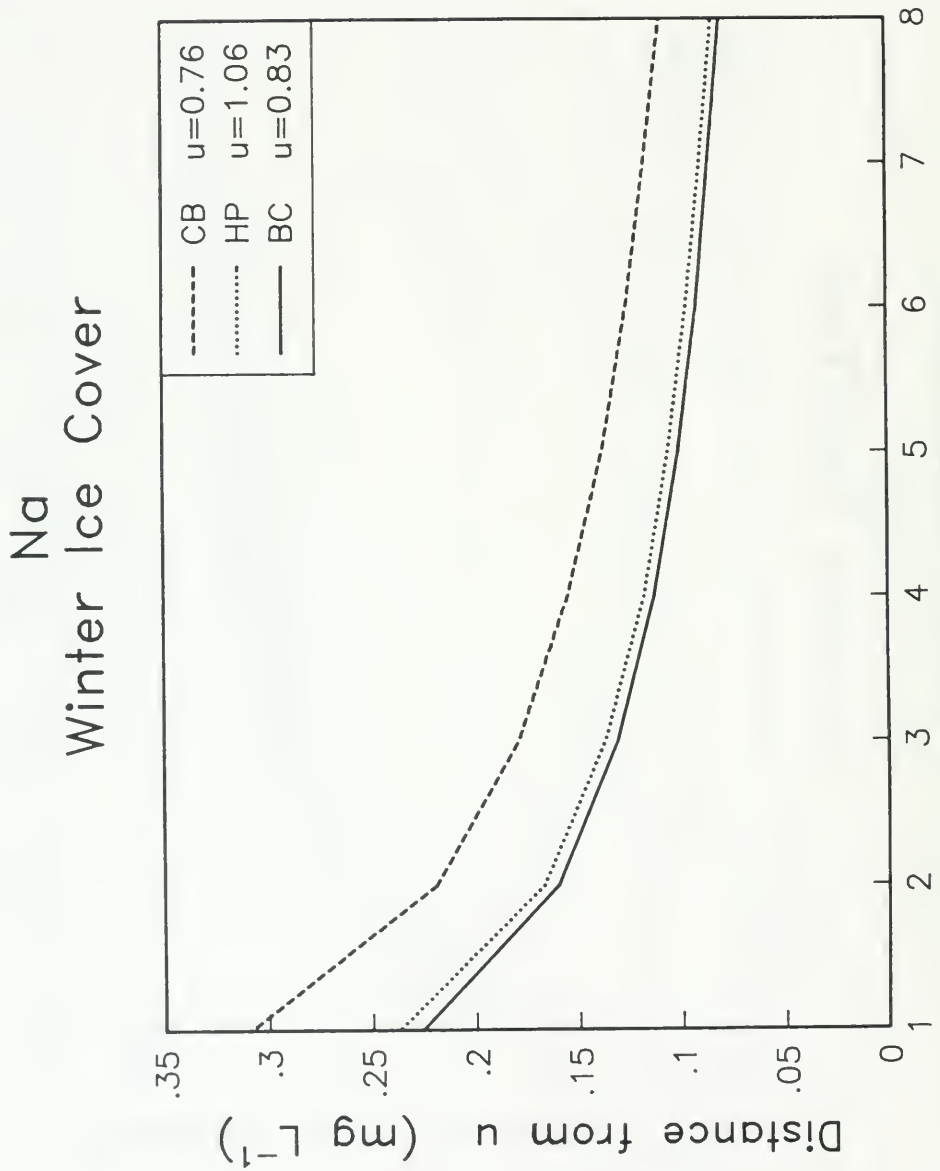
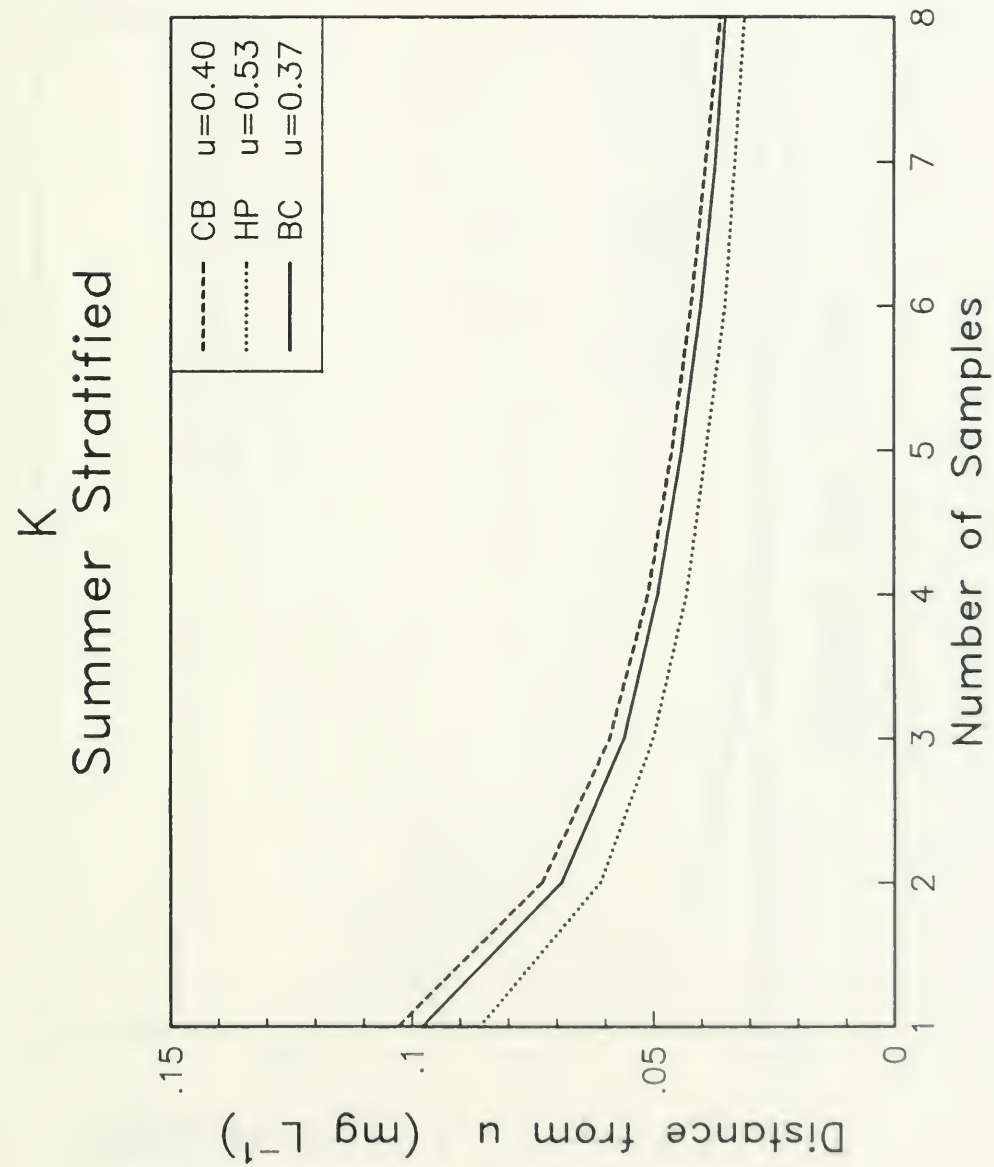

Na
Winter Ice Cover
CB u=0.76
HP u=1.06
BC u=0.83
Distance from u (mg L⁻¹)
.35
.3
.25
.2
.15
.1
.05
0
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.m


K
Summer Stratified
CB u=0.40
HP u=0.53
BC u=0.37
Distance from u (mg L⁻¹)
.15
.1
.05
0
1
2
3
4
5
6
7
8
Number of Samples

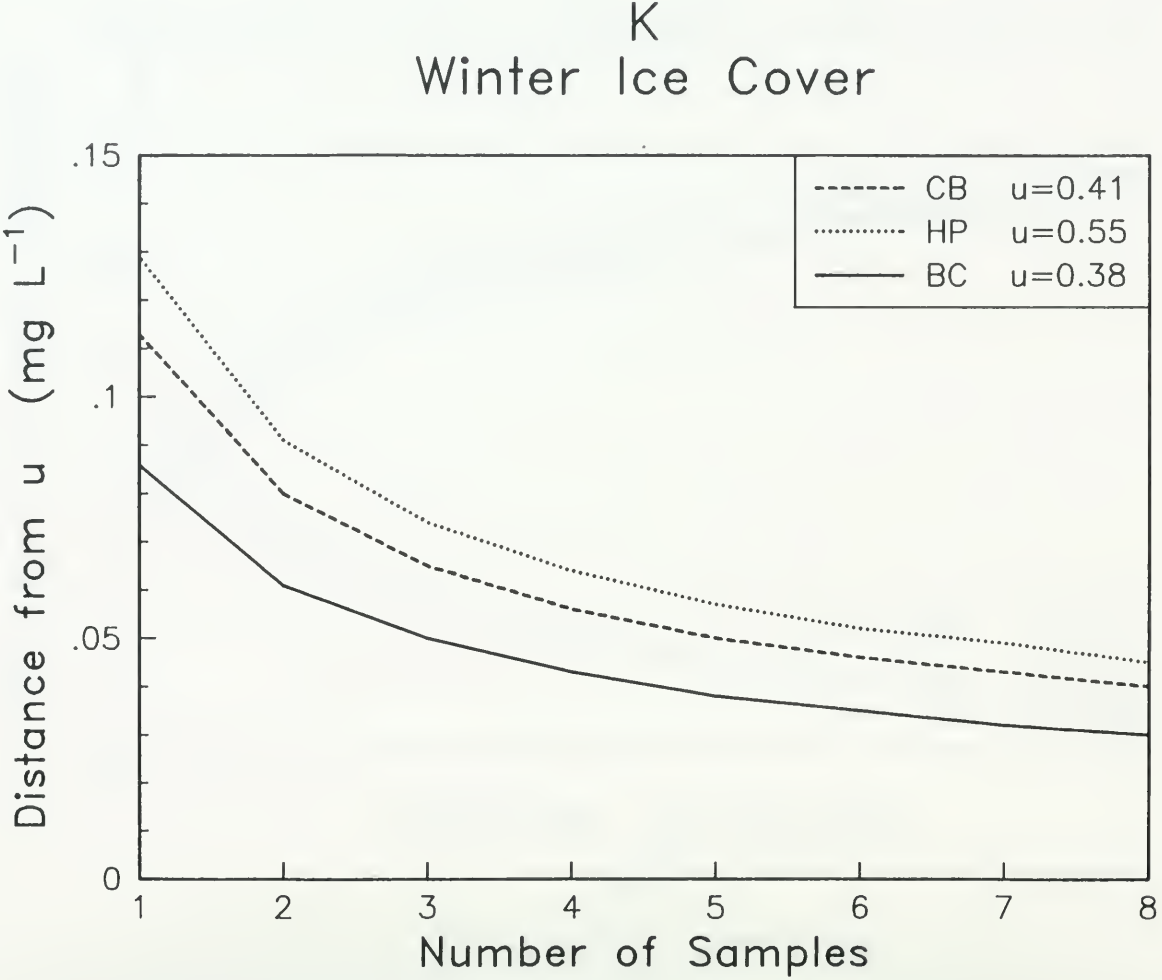

K
Winter Ice Cover
CB u=0.41
HP u=0.55
BC u=0.38
Distance from u (mg L^{-1})
.15
.1
.05
0
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.n

Fig. 7.o

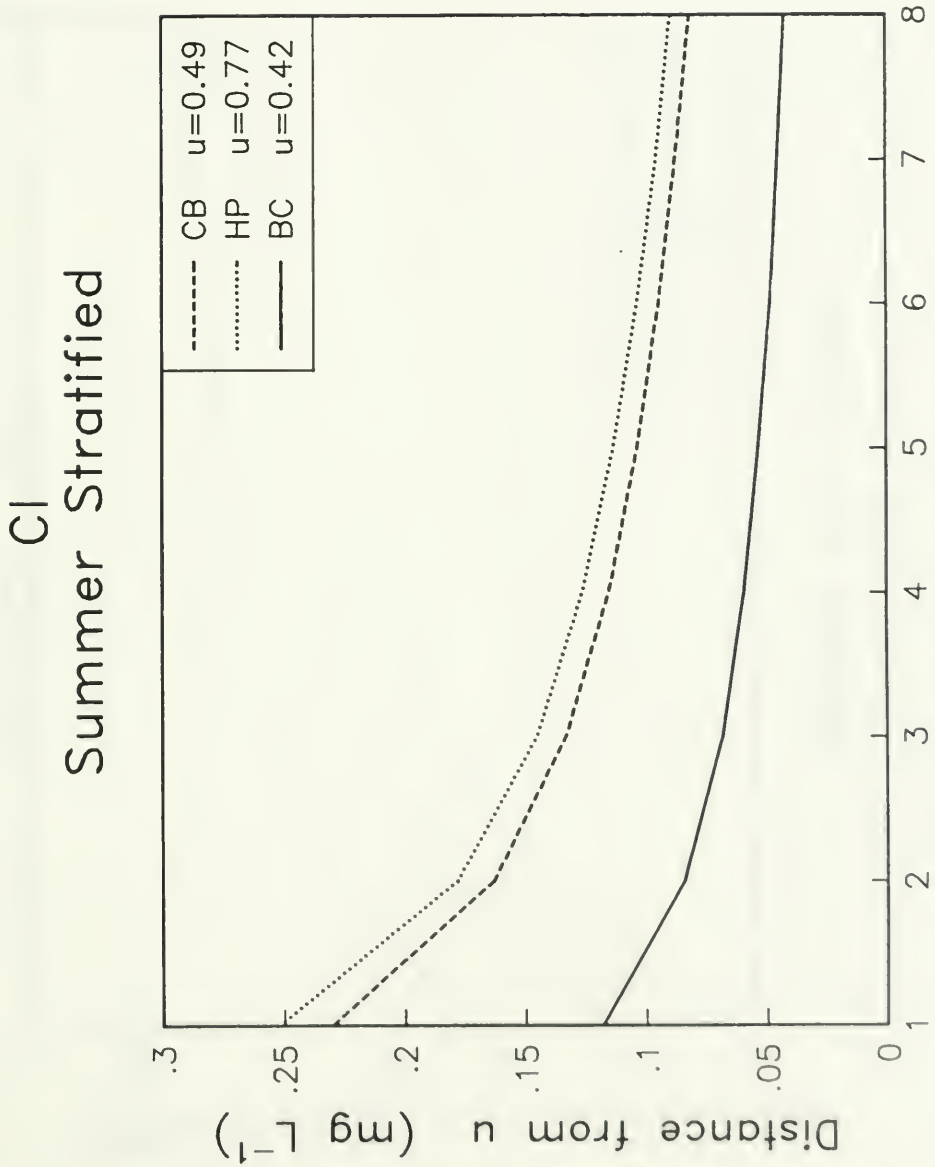

Cl
Summer Stratified
CB u=0.49
HP u=0.77
BC u=0.42
Distance from u (mg L⁻¹)
.3
.25
.2
.15
.1
.05
0
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.p

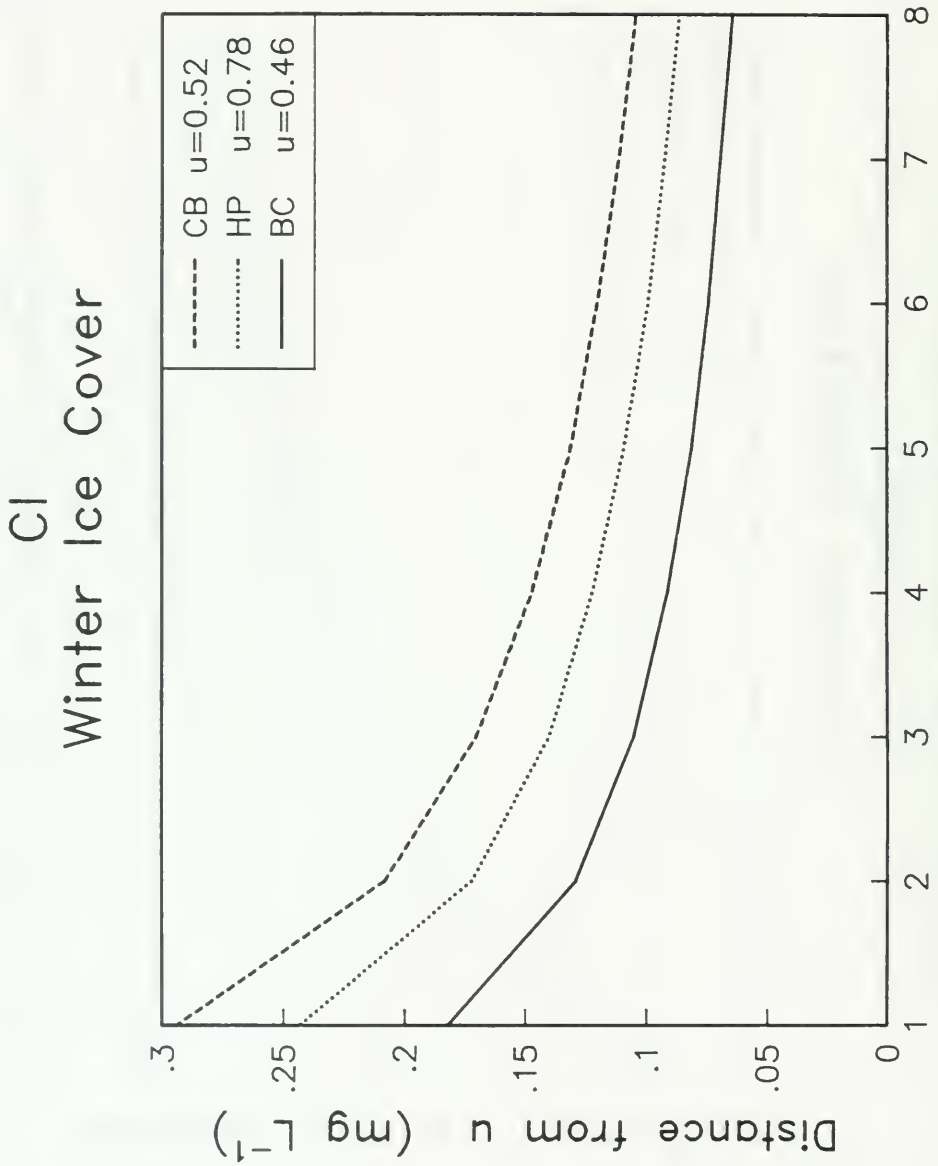

Cl
Winter Ice Cover
CB u=0.52
HP u=0.78
BC u=0.46
Distance from u (mg L⁻¹)
0
.05
.1
.15
.2
.25
.3
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.q

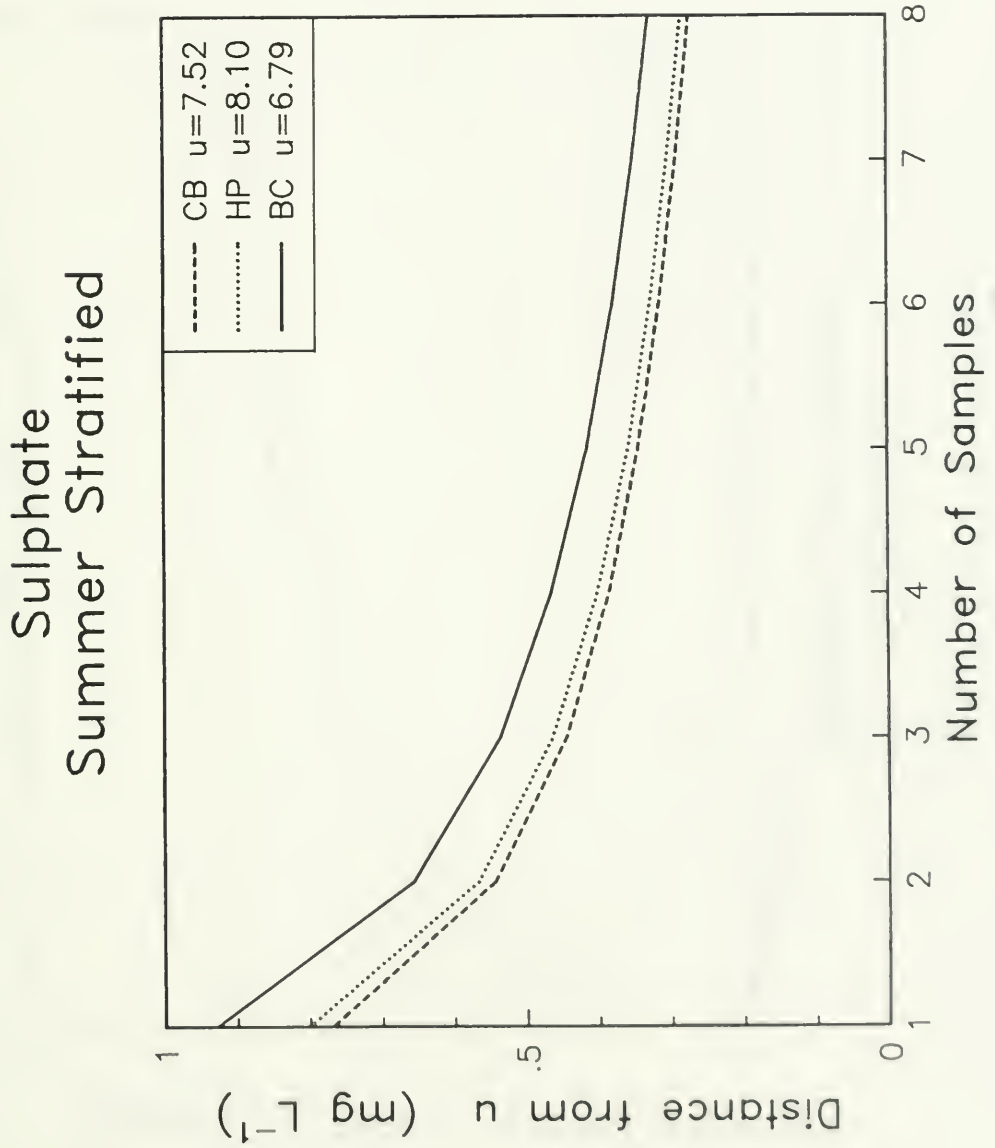

Sulphate
Summer Stratified
CB u=7.52
HP u=8.10
BC u=6.79
Distance from u (mg L⁻¹)
Number of Samples
0
.5
1
1
2
3
4
5
6
7
8

Fig. 7.r

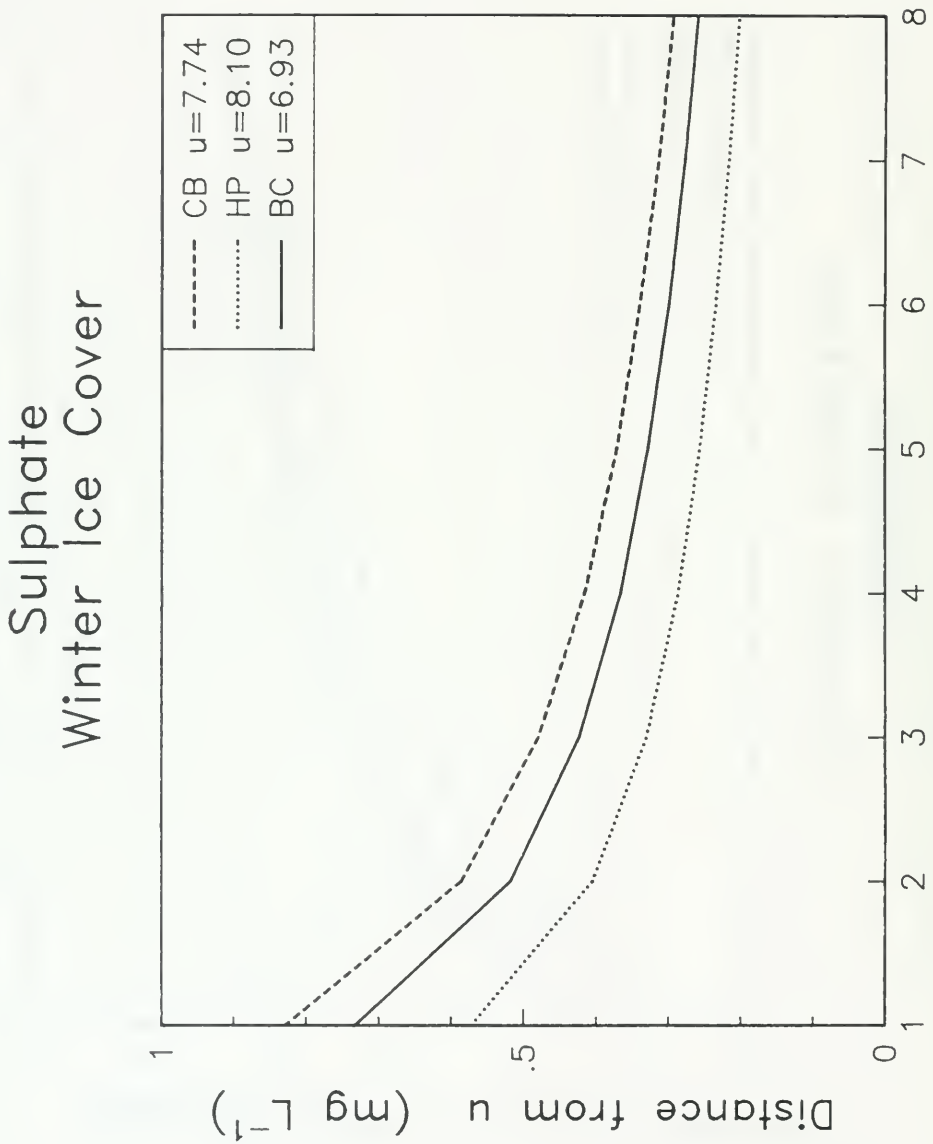

Sulphate
Winter Ice Cover
CB u=7.74
HP u=8.10
BC u=6.93
Distance from u (mg L⁻¹)
1
.5
0
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.s

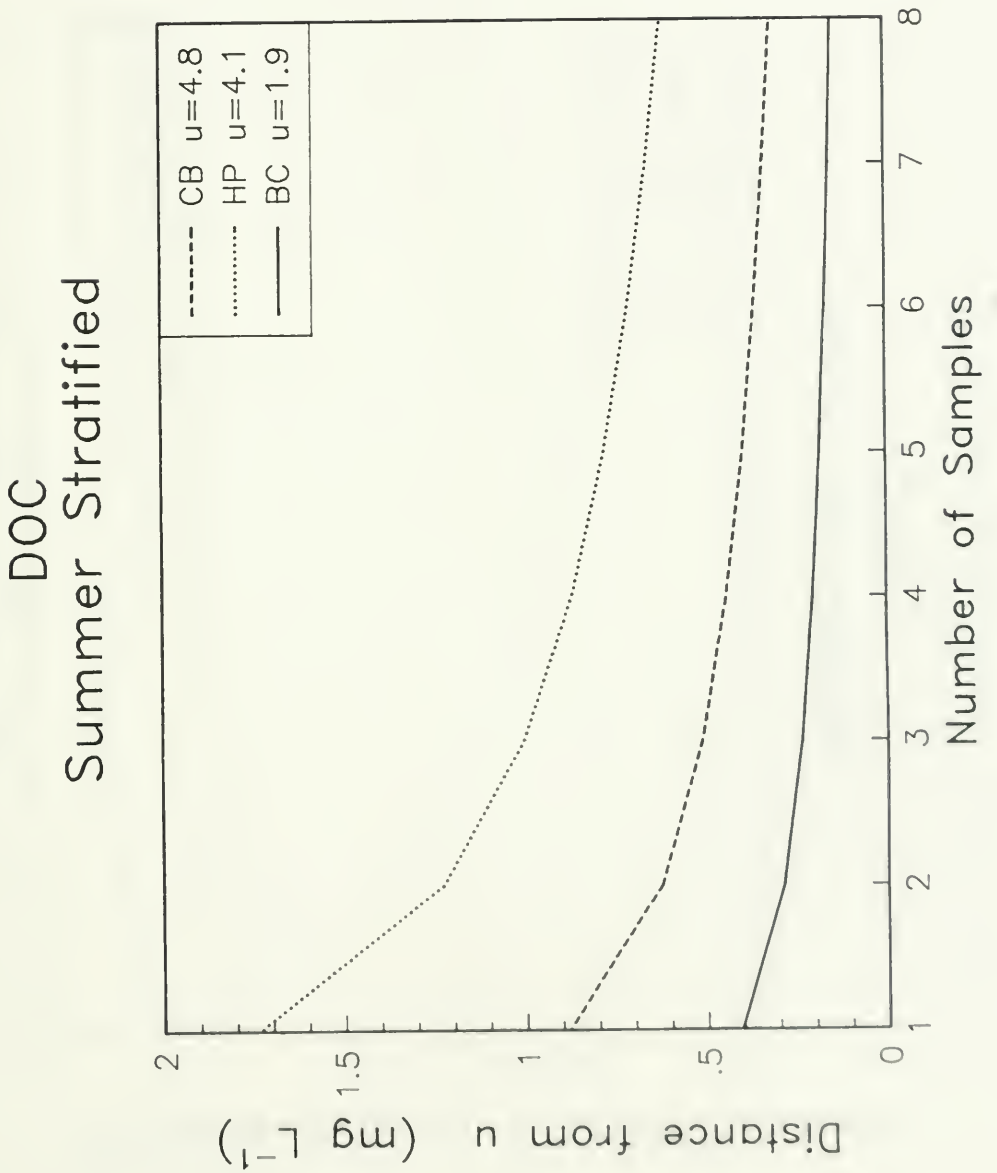

DOC
Summer Stratified
CB u=4.8
HP u=4.1
BC u=1.9
Distance from u (mg L⁻¹)
Number of Samples
0
.5
1
1.5
2
1
2
3
4
5
6
7
8

Fig. 7.t

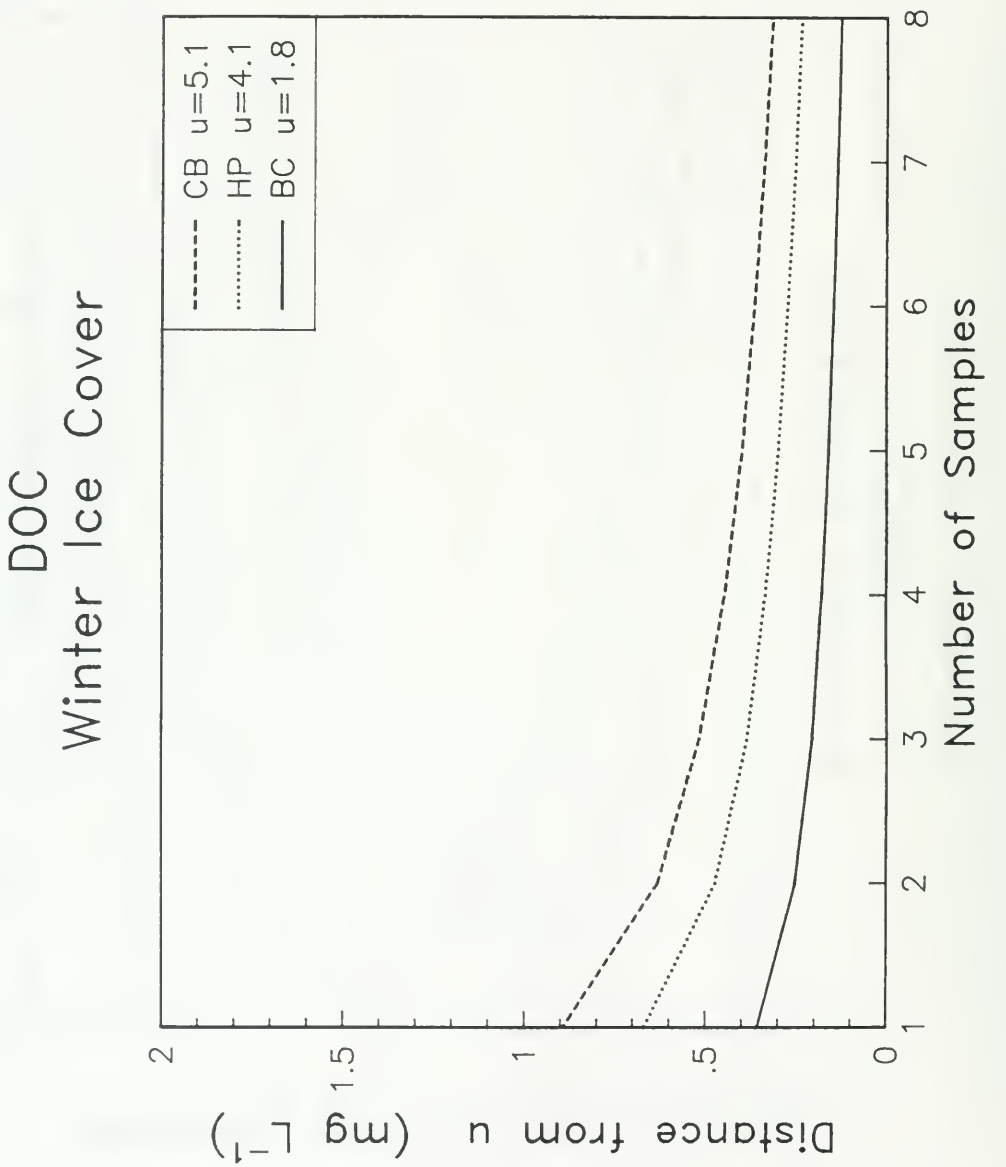

DOC
Winter Ice Cover
CB u=5.1
HP u=4.1
BC u=1.8
Distance from u (mg L⁻¹)
0
.5
1
1.5
2
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.u

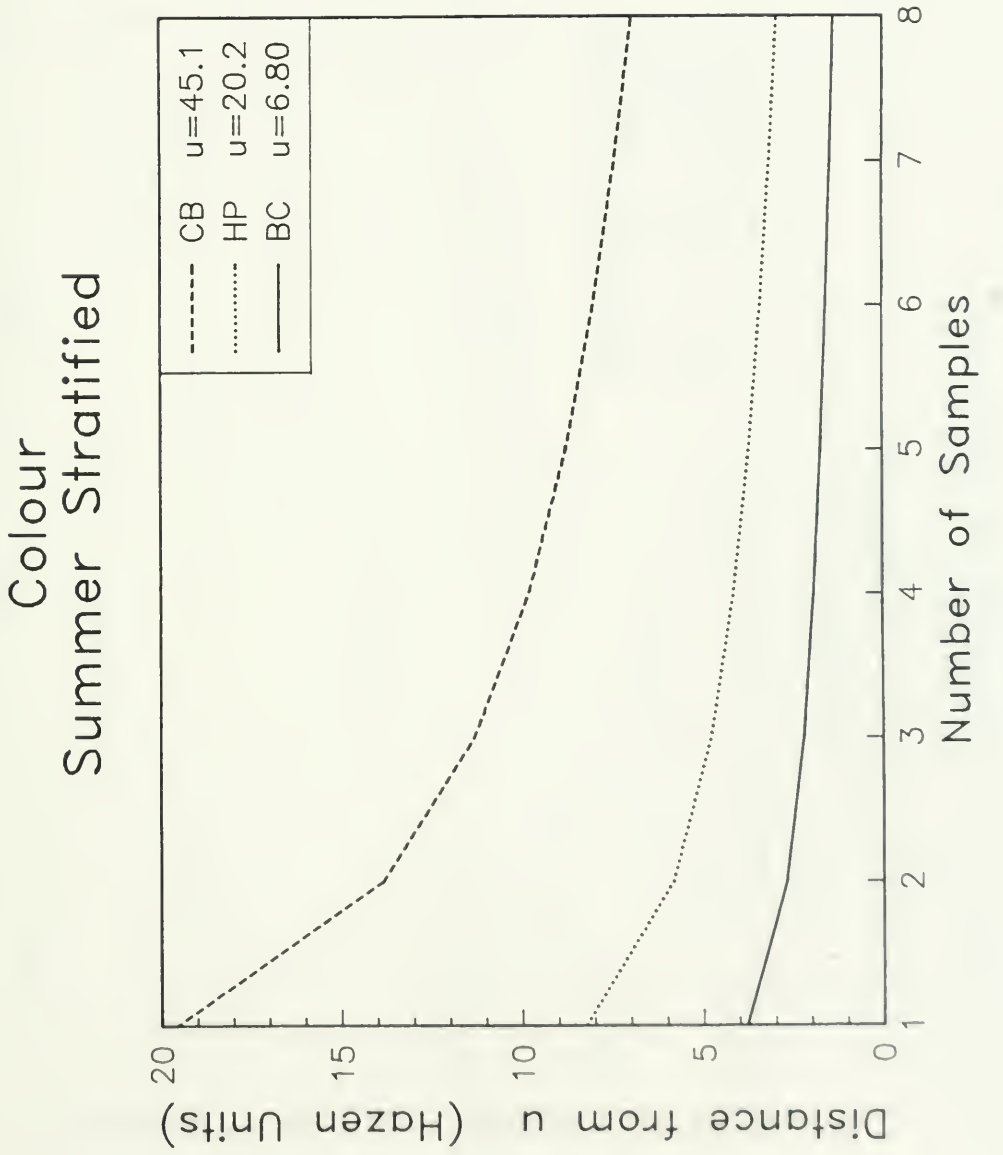

Colour
Summer Stratified
CB u=45.1
HP u=20.2
BC u=6.80
Distance from u (Hazen Units)
0
5
10
15
20
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.v

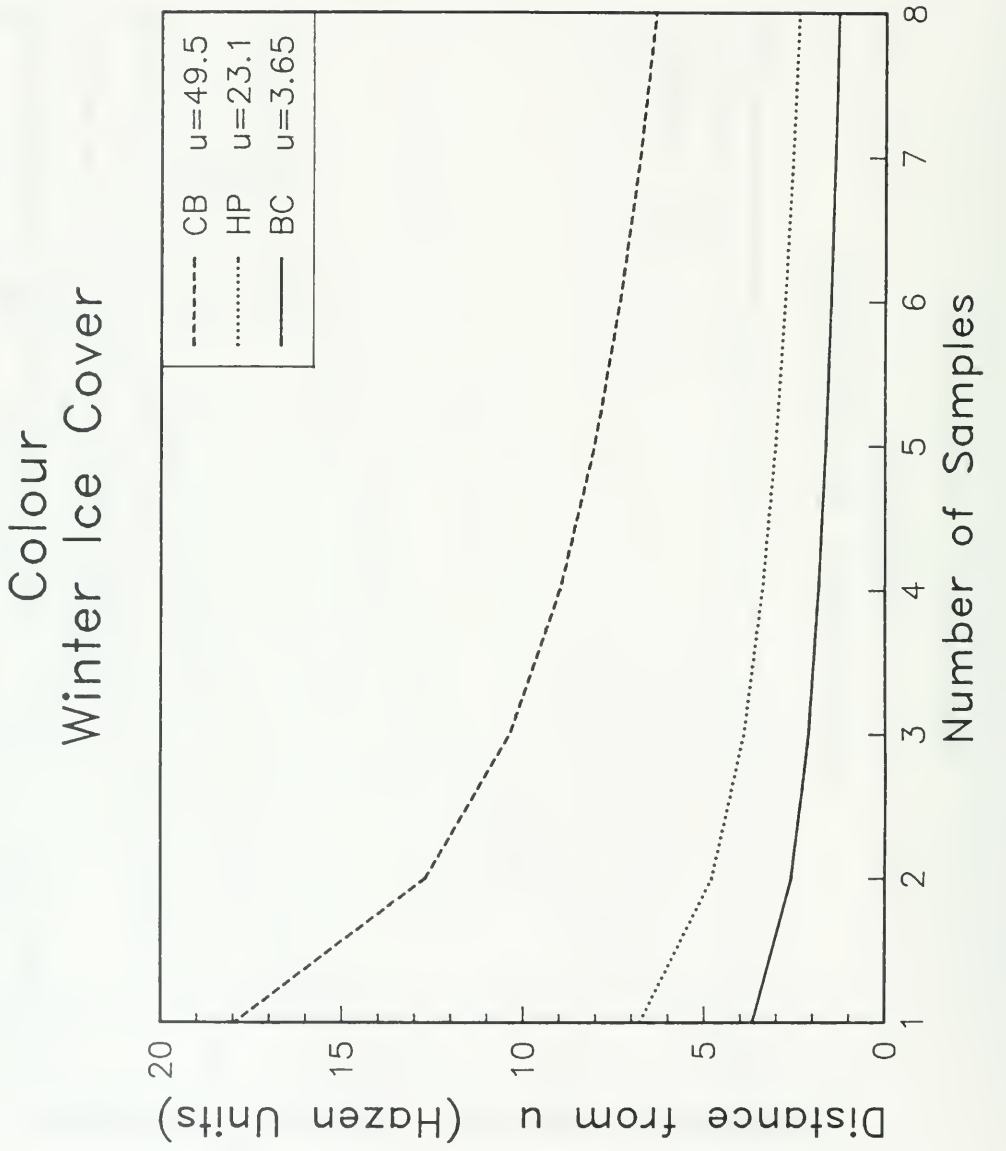

Colour
Winter Ice Cover
CB u=49.5
HP u=23.1
BC u=3.65
Distance from u (Hazen Units)
0
5
10
15
20
1
2
3
4
5
6
7
8
Number of Samples

Fig. 7.w

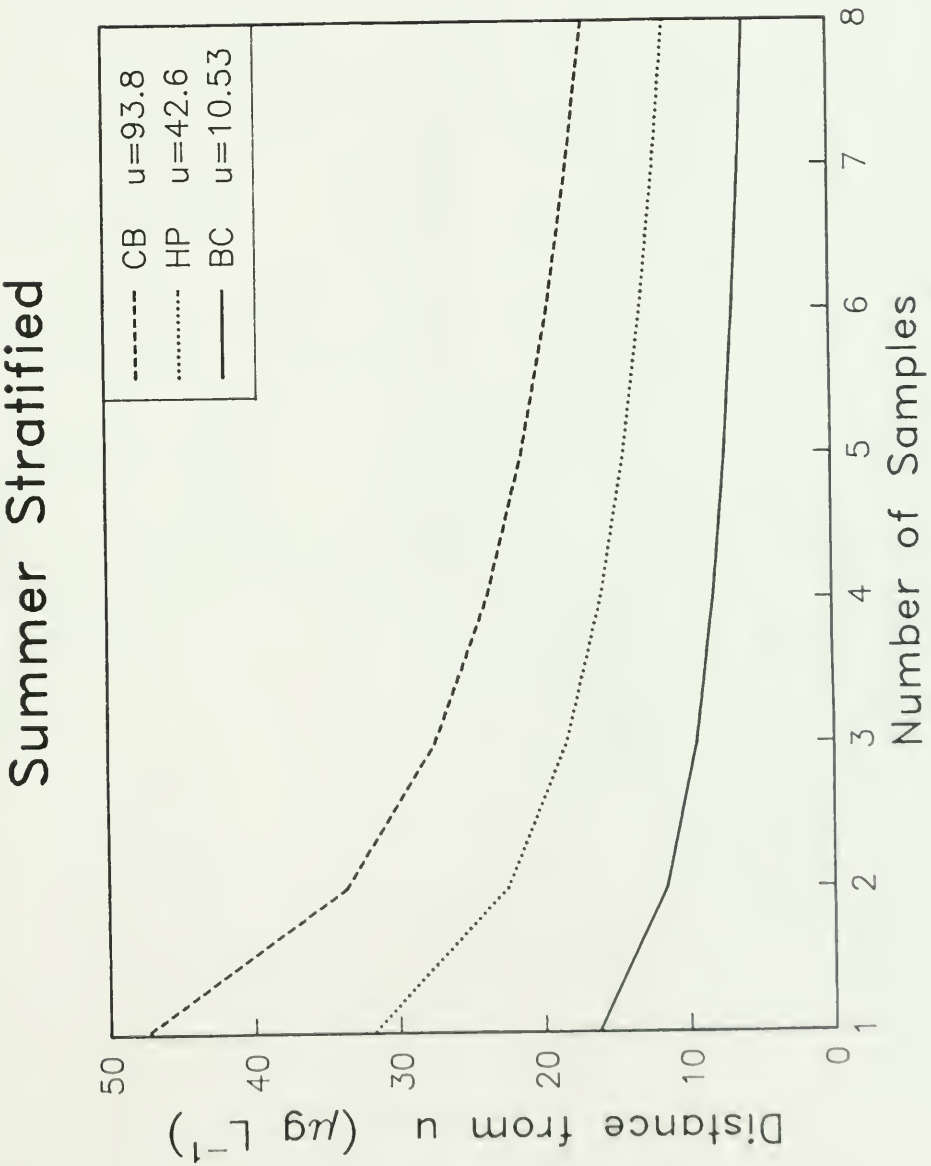
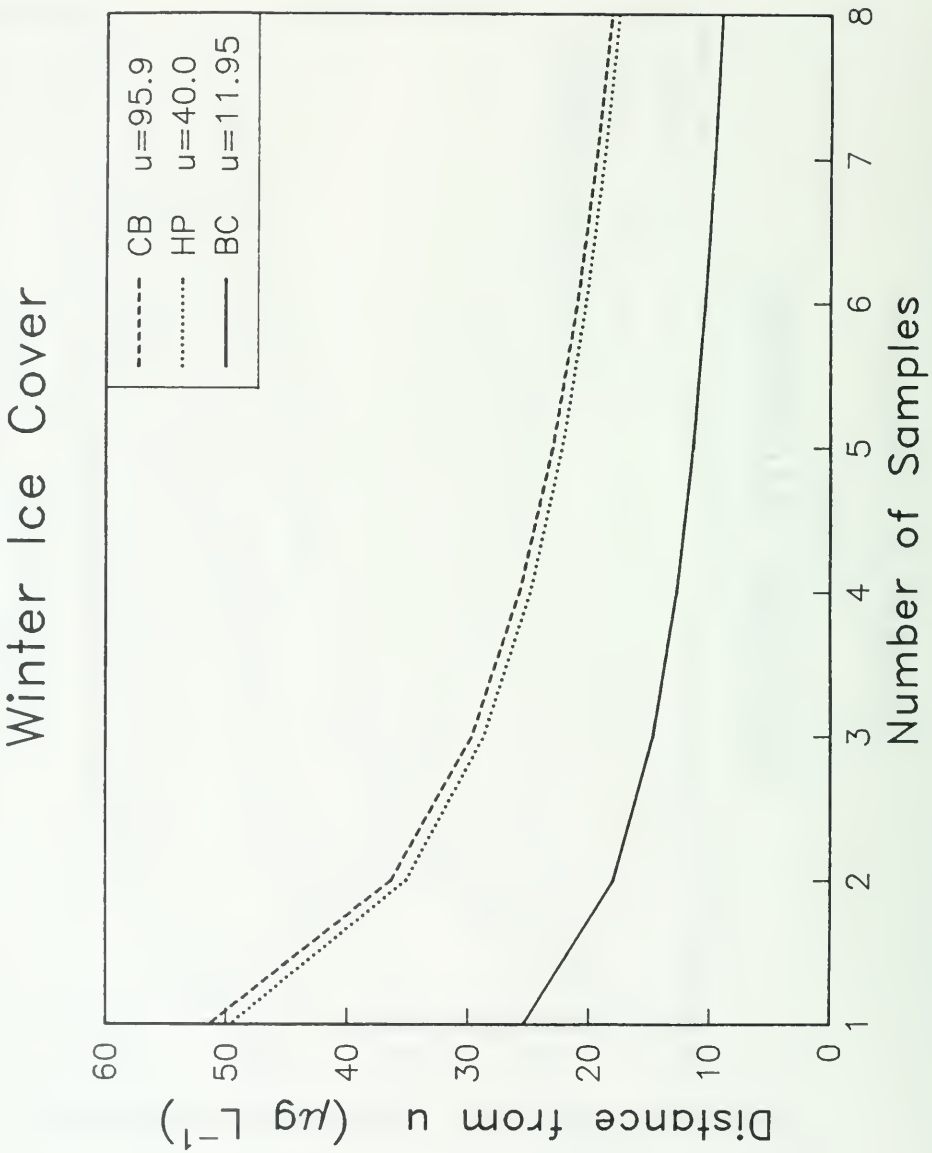

Al
Summer Stratified
CB u=93.8
HP u=42.6
BC u=10.53
Distance from u (μg L⁻¹)
Number of Samples
0
10
20
30
40
50
1
2
3
4
5
6
7
8

Fig. 7.x


Al
Winter Ice Cover
CB u=95.9
HP u=40.0
BC u=11.95
Distance from u (μg L⁻¹)
Number of Samples
0
10
20
30
40
50
60
1
2
3
4
5
6
7
8